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The Nature of the Chemical Bond. VII. The Calculation of Resonance Energy in Conjugated Systems

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The quantum-mechanical treatment previously applied to benzene, naphthalene, and the hydrocarbon free radicals is used in the calculation of extra resonance energy of conjugation in systems of double bonds, the dihydronaphthalenes and dihydroanthracenes, phenylethylene, stilbene, isostilbene, triphenylethylene, tetraphenylethylene, biphenyl, *o*, *m*, and *p*-diphenylbenzene, and 1,3,5-triphenylbenzene. The calculated values, which are in approximate agreement with empirical values from thermochemical data, are used in the discussion of chemical properties and in the formulation of rules regarding conjugation in overlapping systems.

WITH the aid of the recently developed method[1] of calculating matrix elements for various electronic structures of molecules, based on Slater's treatment,[2] we have carried out a quantum-mechanical discussion of a number of conjugated systems involving double bonds and aromatic nuclei. This discussion, which is presented in the following pages, is closely similar to that previously given benzene and anthracene and the hydrocarbon free radicals,[3] and has similarly led to an illuminating qualitative and semi-quantitative explanation of the properties of the systems.

ADDITION PRODUCTS OF NAPHTHALENE

The measurements of heats of combustion made by Roth and Auwers[4] show that liquid 1,2-dihydronaphthalene, in which the benzene ring is conjugated with a double bond, is 4.9 kcal. more stable than liquid 1,4-dihydronaphthalene, in which this conjugation does not occur. It is probable that these isomers differ by about 0.1 kcal. in heat of vaporization, the boiling points being 206.5 and 212.0°C, respectively, leading to a difference in energy of the gaseous molecules of 5.0 kcal. This information permits us to discuss the effect of change in carbon-carbon distance on the exchange integral between adjacent atoms. A canonical set of fourteen independent structures for 1,2-dihydronaphthalene (in all of which single bonds between adjacent atoms are left unchanged) is shown in Fig. 1. Of these the two unexcited structures 1 and 2 will contribute most to the normal state of the molecule, so that the carbon-carbon distance for the 3–4 bond and for the six bonds of the unbroken benzene ring will be the double-bond distance of 1.38A, and the corresponding exchange integral will be that previously[3] designated by the symbol α, and found to have a value of about -1.5 v.e. The carbon-carbon distance connecting the 3–4 bond with the benzene ring

* Contribution No. 370.

[1] Linus Pauling, J. Chem. Phys. **1**, 280 (1933). The same calculations could be made by the use of the method of Eyring and Kimball, J. Chem. Phys. **1**, 239 (1933).

[2] J. C. Slater, Phys. Rev. **38**, 1109 (1931).

[3] Linus Pauling and G. W. Wheland, J. Chem. Phys. **1**, 362 (1933).

[4] W. A. Roth and K. v. Auwers, Liebig's Ann. **407**, 145 (1915).

will be somewhat larger, lying somewhere between 1.38 and 1.54A, inasmuch as the structures which make this bond a double bond are first-excited structures, and hence play a subordinate rôle in the normal state of the molecule. The corresponding exchange integral, which we may designate as β, will thus have a somewhat different value from α (presumably smaller in absolute value). The remaining three carbon-carbon distances will have the single-bond value 1.54A, for neither the unexcited nor the first-excited structures make them double bonds. The corresponding exchange integral β' will hence differ from α by an amount somewhat larger than for β.

If we assume that structures 1 and 2 have the same coefficients in the wave function for the normal state, and similarly 3, 4, 5; 6, 7, 8; 9, 10, 11; and 12, 13, 14, we obtain the following secular equation, in which x represents the quantity $(Q-W')/\alpha$, and b the ratio β/α. The energy $W_{1,2}$ of the molecule is equal to $W'-3/2\beta$, the latter term being omitted in the secular equation for convenience.

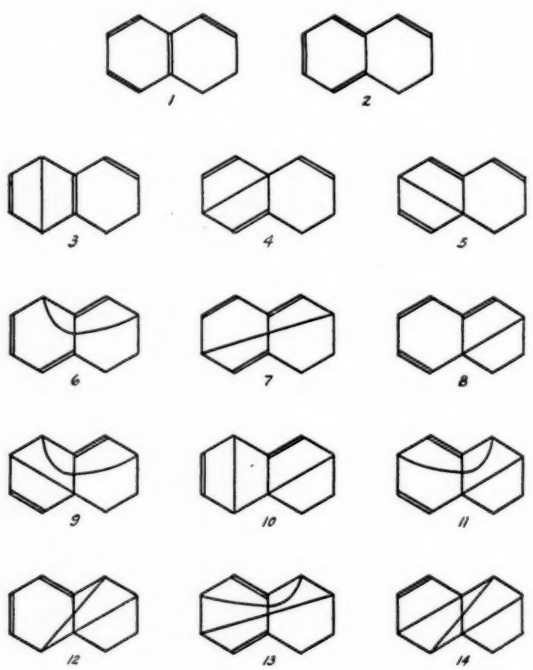

FIG. 1. Complete set of canonical structures for 1,2-dihydronaphthalene.

$$\begin{vmatrix} 5x/2+17/2-5b/4 & 3x+12-3b/2 & 7x/4+25/4+7b/4 & 7x/4+25/4-b/8 & x+4+b \\ 3x+12-3b/2 & 9x/2+27/2-9b/4 & 9x/4+33/4+9b/4 & 9x/4+33/4 & 3x/2+9/2+3b/2 \\ 7x/4+25/4+7b/4 & 9x/4+33/4+9b/4 & 11x/2+7/4+11b/2 & 5x/2+53/8+5b/2 & 5x/2+7/4+5b/2 \\ 7x/4+25/4-b/8 & 9x/4+33/4 & 5x/2+53/8+5b/2 & 11x/2+5/2-11b/4 & 11x/8+4+11b/8 \\ x+4+b & 3x/2+9/2+3b/2 & 5x/2+7/4+5b/2 & 11x/8+4+11b/8 & 5x/2-11/4+5b/2 \end{vmatrix} = 0.$$

Because of the small contribution of the second and third-excited states, we may neglect them, which reduces the equation to a cubic, of the form

$$b^2(198z-63)+b(234z^2+132z-390) +(68z^3+44z^2-884z-582)=0, \quad (1)$$

in which $z=-x-b$.

If as an approximation we assume $b=1(\beta=\beta'=\alpha)$, we find as the pertinent root of this equation $z=2.3062$, corresponding to $W_{1,2}=Q+1.8062\alpha$. A similar treatment applied to 1,4-dihydrobenzene (which involves no interaction between the benzene ring and the double bond) leads to $W_{1,4}=Q+3.6055\alpha-2\beta'$, or, in this case, $Q+1.6055\alpha$. (In this paper as in the previous one interactions involving the single bonds between adjacent atoms are neglected, on the reasonable assumption that they are effectively the same for all the structures considered.) Hence the 1,2 compound is calculated to be more stable than the 1,4 compound by -0.2007α or, for $\alpha=-1.5$ v.e., 0.301 v.e. This is in rough agreement with the experimental value 5.0 kcal. or 0.22 v.e. given above. The comparison indicates that β and β' differ from α by a few percent. If we assume, as is reasonable because of the relative interatomic distances, that β lies midway between β' and α, and that a safe lower limit for the extra stability of the 1,2 compound is 4.6 kcal. or -0.14α, we write as a second equation connecting b and z

$$z=4.2455-2b. \quad (2)$$

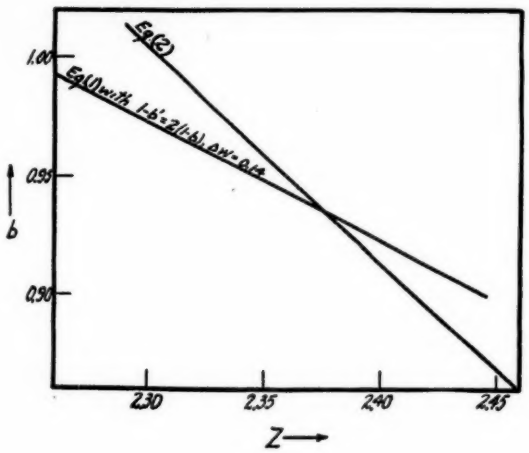

FIG. 2.

The simultaneous solution of Eqs. (1) and (2) is shown in Fig. 2, in which the two curves represent the two relations between the variables. Their intersection corresponds to $\beta=0.935\alpha$ and $\beta'=0.87\alpha$, which are thus minimum values for these exchange integrals.

It is probable that the errors introduced by the neglect of all except unexcited and first-excited structures and by equating β and β' to α cancel each other to a considerable extent, especially for more complicated molecules than the dihydronaphthalenes. These approximations are made throughout the rest of this paper.

Calculated resonance energies for $1,2-C_{10}H_{10}$, $1,4-C_{10}H_{10}$, $1,5-C_{10}H_{10}$, and $9,10-C_{10}H_{10}$, the last two involving a chain of four and two chains of two conjugated double bonds (discussed in a following section), are given in Table I. No data are available regarding the two least stable dihydronaphthalenes.

TABLE I. *Calculated resonance energies for dihydronaphthalenes.*

	W	$W-W_{1,2}$	$W-W_{1,2}$
$1,2-C_{10}H_{10}$	$Q+1.8062\alpha$	0	0
$1,4-C_{10}H_{10}$	$Q+1.6055\alpha$	-0.2007α	0.301 v.e.
$1,5-C_{10}H_{10}$	$Q+1.225\alpha$	-0.581α	0.872
$9,10-C_{10}H_{10}$	$Q+0.964\alpha$	-0.842α	1.263

ADDITION PRODUCTS OF ANTHRACENE

The secular equation for 1,2-dihydroanthracene resulting from the consideration of (I) the symmetrical unexcited structure, (II) the two unsymmetrical unexcited structures, (III) the sixteen first-excited structures not involving conjugation of the double bond and the naphthalene nucleus, and (IV) the six first-excited structures involving this conjugation, is

$$\begin{vmatrix} x+5/2 & x/2+7/2 & 35x/8+361/16 & 19x/16+7 \\ x/2+7/2 & 17x/8+103/16 & 19x/2+47 & 35x/16+403/32 \\ 35x/8+361/16 & 19x/2+47 & 557x/8+4627/16 & 427x/32+2599/32 \\ 19x/16+7 & 35x/16+403/32 & 427x/32+2599/32 & 119x/8+595/16 \end{vmatrix} = 0.$$

The pertinent root of this is $x=-4.599$, corresponding to the energy $W_{1,2}=Q-x\alpha-3\alpha/2=Q+3.099\alpha$, of which $Q+2.976\alpha$ results from resonance within the naphthalene nucleus (calculated by neglecting all structures other than the three unexcited and the sixteen naphthalene first-excited structures), and the difference, 0.123α, is the energy of conjugation of the naphthalene nucleus and the double bond. The total energy of 1,4-dihydroanthracene, in which this conjugation does not occur, is $W_{1,4}=Q+2.976\alpha$, and that of 9,10-dihydroanthracene, involving two unconjugated benzene rings, is $W_{9,10}=Q+3.190\alpha$ (Table II). Table II could be easily extended to include additional less stable and as yet unprepared dihydroanthracenes and higher addition products. No thermal data are available for comparison with the calculated energy values of Table II.

TABLE II. *Calculated resonance energies for dihydroanthracenes.*

	W	$W-W_{9,10}$	$W-W_{9,10}$
$9,10-C_{14}H_{12}$	$Q+3.190\alpha$	0	0
$1,2-C_{14}H_{12}$	$Q+3.099\alpha$	-0.091α	0.137 v.e.
$1,4-C_{14}H_{12}$	$Q+2.976\alpha$	-0.214α	0.321 v.e.

The resonance energies are essentially independent of the nature of the atoms attached to the nucleus; hydrogen is mentioned for convenience.

It is, however, reasonable to assume that, in the case of closely similar reactions, that reaction leading to the most stable product will occur most easily. This hypothesis leads to a complete explanation of the observed courses of hydrogenation of benzene, naphthalene, and anthracene, which are represented by the following schemes, showing only the reactions for which data are available.[5]

$$C_6H_6+H_2\rightarrow 1,2-C_6H_8+H_2$$
$$\rightarrow 1,2,3,4-C_6H_{10}+H_2\rightarrow C_6H_{12}.$$

$$C_{10}H_8+H_2\rightarrow 1,2-C_{10}H_{10}+H_2\rightarrow 1,2,3,4-C_{10}H_{12}.$$

$$C_{14}H_{10}+H_2\rightarrow 9,10-C_{14}H_{12}+H_2$$
$$\rightarrow 1,2,3,4-C_{14}H_{14}+2H_2$$
$$\rightarrow 1,2,3,4,5,6,7,8-C_{14}H_{18}+3H_2\rightarrow C_{14}H_{24}.$$

With this hypothesis, the calculated stability of the 9,10 addition compound of anthracene provides an explanation of the ease of attack of the 9,10 positions for addition. A similar calculation for phenanthrene shows that for this molecule too the 9,10 positions should be most reactive.

Conjugated Double-Bond Systems

In Table III are given calculated values of the resonance energy for straight conjugated chains containing two, three, and four double bonds and a branched chain with three double bonds (the list could be easily extended). In each case the secular equation was solved as a quadratic, all first-excited structures being given the same coefficient. No reliable thermochemical data are available for comparison with these values. It may be mentioned that our hypothesis provides no information regarding addition in various positions (1,2 *vs.* 1,4 in dienes), which must instead be discussed on the basis of detailed mechanisms.

Table III. *Resonance energies in systems of double bonds.*

System	Number of first-excited structures	Resonance energy
= – =	1	$-0.232\alpha=0.348$ v.e.
= – = – =	3	$-0.482\alpha=0.723$ v.e.
= – = – = – =	6	$-0.725\alpha=1.09$ v.e.
	2	$-0.438\alpha=0.657$ v.e.

[5] W. Hückel, *Theoretische Grundlagen der organischen Chemie*, 1, p. 359, Akad. Verlag. M. B. H., Leipzig, 1931.

Phenylethylene, Stilbene, etc.

The secular equation for phenylethylene, in which a phenyl group is conjugated with a double bond, is the same as for 1,2-dihydronaphthalene, and leads to the same value for the resonance energy.

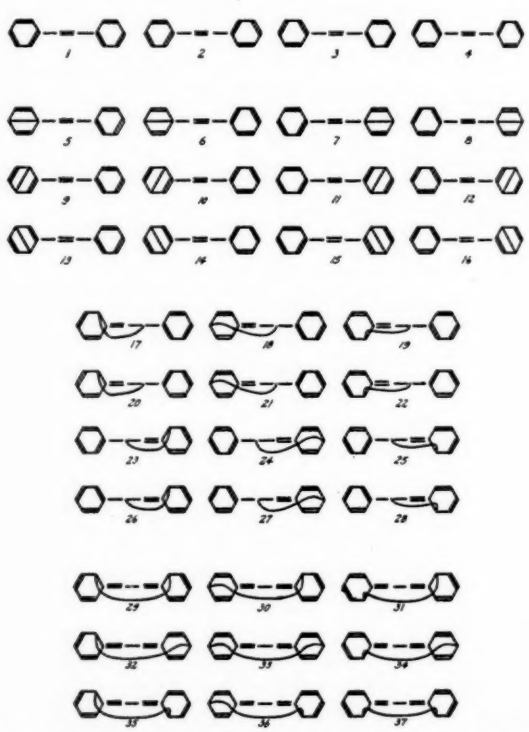

Fig. 3. Unexcited and first-excited canonical structures of sym.-diphenylethylene.

For stilbene, sym.-diphenylethylene, we consider the thirty-seven structures shown in Fig. 3, grouping together the four unexcited structures, the twelve first-excited structures not involving conjugation, the twelve in which there is conjugation of the double bond and a phenyl group, and the nine in which there is conjugation of the two phenyl groups by way of the double bond. This leads to the biquadratic secular equation

$$\begin{vmatrix} 25x/4+30 & 15x+81 & 35x/4+453/8 & 49x/16+399/16 \\ 15x+81 & 81x/2+207 & 87x/4+1185/8 & 63x/8+519/8 \\ 35x/4+453/8 & 87x/4+1185/8 & 269x/8+1107/8 & 77x/4+753/8 \\ 49x/16+399/16 & 63x/8+519/8 & 77x/4+753/8 & 121x/4+759/8 \end{vmatrix} = 0,$$

which on solution as a biquadratic leads to $W=Q+5.5889\alpha$. The energy the molecule would have without resonance, found by equating the upper left-hand quadratic part of the secular determinant to zero, is $W'=Q+5.1898\alpha$, corresponding to an extra resonance energy of conjugation of 0.3891α.

The secular equation for isostilbene, in which there is no conjugation of the two phenyl groups with each other, is just the cubic equation obtained from the stilbene determinant by omitting the fourth row and column.

The secular equation for triphenylethylene, corresponding to 8, 36, 36, and 36 structures of the four kinds described for stilbene, is

$$\begin{vmatrix} 125x/8+1675/16 & 225x/4+3285/8 & 525x/16+4395/16 & 245x/16+4921/32 \\ 225x/4+3285/8 & 1755x/8+25,569/16 & 1935x/16+17,019/16 & 231x/4+2379/4 \\ 525x/16+4395/16 & 1935x/16+17,019/16 & 2385x/16+31,653/32 & 3423x/32+12,465/16 \\ 245x/16+4921/32 & 231x/4+2379/4 & 3423x/32+12,465/16 & 2959x/16+3985/4 \end{vmatrix} = 0.$$

That for tetraphenylethylene, with 16, 96, 196, and 144 structures, respectively, of these four kinds, is

$$\begin{vmatrix} 625x/16+5375/16 & 375x/2+1725 & 875x/8+17,975/16 & 1225x/16+7315/8 \\ 375x/2+1725 & 3825x/4+35,685/4 & 4275x/8+91,815/16 & 3045x/8+18,699/4 \\ 875x/8+17,975/16 & 4275x/8+91,815/16 & 9175x/16+41,245/8 & 12,845x/32+273,911/64 \\ 1225x/16+7315/8 & 3045x/8+18,699/4 & 12,845x/32+273,911/64 & 74,761x/64+557,465/64 \end{vmatrix} = 0.$$

The energy values obtained on solution of these equations are given in Table IV.

Conjugated Benzene Rings

For biphenyl we consider four unexcited structures, twelve first-excited structures not involving conjugation, and nine involving conjugation, as shown in Fig. 4. These lead to the secular equation

$$\begin{vmatrix} 25x/4+215/8 & 15x+147/2 & 49x/8+301/8 \\ 15x+147/2 & 81x/2+747/4 & 63x/4+393/4 \\ 49x/8+301/8 & 63x/4+393/4 & 121x/4+319/4 \end{vmatrix} = 0,$$

whose solution is given in Table V.

For ortho, meta, and para diphenylbenzene we consider eight unexcited structures of the type indicated by the letter A in Fig. 5, thirty-six first-excited structures of type B, and thirty-six of type C, in which there is conjugation with the central ring. This includes all first-excited structures for m-diphenylbenzene. For ortho and para diphenylbenzene, however, there are in addition nine first-excited structures of type D, in which the two end rings are conjugated together. The secular equation for the ortho compound is

$$\begin{vmatrix} 125x/8+775/8 & 225x/4+765/2 & 245x/8+3941/16 & 245x/64+1169/32 \\ 225x/4+765/2 & 1755x/8+11,907/8 & 231x/2+1917/2 & 231x/16+4527/32 \\ 245x/8+3941/16 & 231x/2+1917/2 & 5771x/32+7813/8 & 539x/16+3367/16 \\ 245x/64+1169/32 & 231x/16+4527/32 & 539x/16+3367/16 & 121x/4+110 \end{vmatrix} = 0.$$

The secular equation for the meta compound is obtained from this by omitting the fourth row and column. That for the para compound is:

$$\begin{vmatrix} 125x/8+775/8 & 225x/4+765/2 & 245x/8+3941/16 & 49x/16+497/16 \\ 225x/4+765/2 & 1755x/8+11,907/8 & 231x/2+1917/2 & 399x/32+981/8 \\ 245x/8+3941/16 & 231x/2+1917/2 & 2959x/16+16,151/16 & 77x/2+1891/8 \\ 49x/16+497/16 & 399x/32+981/8 & 77x/2+1891/8 & 121x/4+110 \end{vmatrix} = 0.$$

For 1,3,5-triphenylbenzene, with 16 unexcited, 96 unconjugated first-excited, and 108 conjugated first-excited structures, the secular equation is

$$\begin{vmatrix} 625x/16+10,125/32 & 375x/2+6525/4 & 3675x/32+9135/8 \\ 375x/2+6525/4 & 3825x/4+67,545/8 & 9135x/16+23,481/4 \\ 3675x/32+9135/8 & 9135x/16+23,481/4 & 50,265x/64+799,227/128 \end{vmatrix} = 0.$$

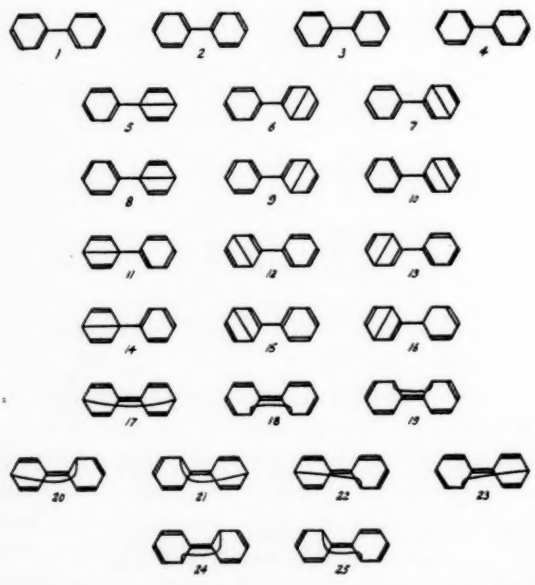

FIG. 4. Unexcited and first-excited structures of biphenyl.

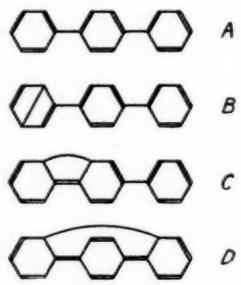

FIG. 5.

TABLE IV. *Calculated resonance energies for phenyl-substituted ethylenes.*

Molecule	W	W'	$W'-W$
Phenylethylene	$Q+3.3062\alpha$	$Q+3.1055\alpha$	$-0.2007\alpha = 0.301$ v.e.
Sym. diphenylethylene	$Q+5.589\alpha$	$Q+5.190\alpha$	$-0.389\alpha = 0.584$ v.e.
Unsym. diphenylethylene	$Q+5.545\alpha$	$Q+5.190\alpha$	$-0.355\alpha = 0.533$ v.e.
Triphenylethylene	$Q+7.804\alpha$	$Q+7.285\alpha$	$-0.519\alpha = 0.779$ v.e.
Tetraphenylethylene	$Q+10.080\alpha$	$Q+9.362\alpha$	$-0.719\alpha = 1.08$ v.e.

The energy values found on solution of these equations and of the non-conjugated parts of them, together with their differences, the energy of conjugation, are given in Table V.

TABLE V. *Calculated resonance energies for conjugated benzene rings.*

Molecule	W	W'	$W'-W$
Biphenyl	$Q+4.867\alpha$	$Q+4.690\alpha$	$-0.177\alpha=0.266$ v.e.
m-Diphenylbenzene	$Q+7.086\alpha$	$Q+6.785\alpha$	$-0.301\alpha=0.452$ v.e.
p-Diphenylbenzene	$Q+7.094\alpha$	$Q+6.785\alpha$	$-0.309\alpha=0.464$ v.e.
o-Diphenylbenzene	$Q+7.103\alpha$	$Q+6.785\alpha$	$-0.318\alpha=0.477$ v.e.
1,3,5-Triphenylbenzene	$Q+9.273\alpha$	$Q+8.862\alpha$	$-0.411\alpha=0.617$ v.e.

COMPARISON WITH EXPERIMENT

The meager existant results of experiments on heats of combustion, given in the previous paper of this series,[6] are in rough agreement with the theoretical calculations, the discrepancies in most cases lying within the experimental error. The calculated energy of conjugation of a benzene ring and a double bond, 0.30 v.e., is in excellent agreement with the extra resonance energy 0.29 v.e. for phenylethylene. For stilbene and isostilbene[7] the empirical values 0.67 and 0.45 v.e. agree less well with the calculated values 0.58 and 0.53 v.e., respectively. For biphenyl the agreement is good, 0.35 v.e. empirical, 0.27 v.e. calculated; for 1,3,5-triphenylbenzene the difference of 0.5 v.e. between the empirical value 1.1 v.e. and the calculated value 0.62 v.e., while large, may be due to error in the reported heat of combustion or in part in the estimated heat of sublimation.

CONCLUSIONS REGARDING CONJUGATION

The calculations provide us with sufficient information to permit the formulation with considerable confidence of a set of rules regarding conjugation.

A phenyl group is 20 or 30 percent less effective in conjugation than a double bond, and a naphthyl group is less effective than a phenyl group. Thus the resonance energy of biphenyl is only 77 percent of that for two conjugated double bonds, and the ratios of energy of conjugation of a double bond with another double bond, a phenyl group, and a naphthyl group are 1 : 0.86 : 0.53.

If a conjugated system can be resolved into two overlapping parts with a common double bond or benzene ring, and with no conjugation from one part to the other by way of the double bond or benzene ring, the total conjugation energy is 10 or 15 percent less than the sum of the conjugation energies for the two parts. Examples are isostilbene, with conjugation energy 1.77 times that for phenylethylene, metadiphenylbenzene, 1.70 times the biphenyl energy, and branched triene, 1.89 times the diene energy. The conjugation energy of 1,3,5-triphenylbenzene, in which the central benzene ring forms a part of three biphenyl systems, is 23 percent less than three times the biphenyl conjugation energy.

In an overlapping system in which there is conjugation from one part to another by way of a double bond this extra conjugation may counteract the effect of overlapping, so that the total conjugation energy is approximately equal to the sum for the parts. Thus the conjugation energy of stilbene is 1.94 times that for phenylethylene, that for unbranched triene 2.08 times that for diene, and for unbranched tetraene 3.12 times that for diene. A phenyl group is not so effective as a link in a conjugated chain, however; no doubt for the reason that, because of resonance between the two Kekulé structures, the average path between ortho or para positions is three bonds long. In consequence the conjugation energy for *p*-diphenylbenzene is only three percent greater than for the meta compound, and that for the ortho compound (in which the bridge is more effective) only six percent greater.

Conjugation of phenyl groups and double bonds is of quite appreciable effect in stabilizing molecules, as is, of course, evident from the early recognition of the phenomenon by chemists. The extra resonance energy of tetraphenylethylene, amounting to 1.08 v.e., is more than enough to overcome the unsaturation of the double bond, amounting to 0.74 v.e. (the difference in energy of two carbon-carbon single bonds and a double bond), in consequence of which the properties of the substance differ radically from those of an

[6] L. Pauling and J. Sherman, J. Chem. Phys. **1**, 606 (1933).

[7] The value for this compound, omitted from the previous paper, is calculated from the heat of combustion by the methods described there.

unsaturated compound such as ethylene.[8] Using the bond-energy values given in earlier papers,[9] we calculate for ΔH for the reactions $C_2(C_6H_5)_4 + X_2 \rightarrow C_2(C_6H_5)_4X_2$ the values -0.30 v.e., -0.42 v.e., and $+0.24$ v.e. for $X_2 = H_2$, Cl_2, and Br_2, respectively. Assuming that ΔF and ΔH do not differ greatly, these values suggest that tetraphenylethylene will add hydrogen and chlorine but not bromine.[10] This is in agreement with experiment; tetraphenylethylene has been hydrogenated catalytically to tetraphenylethane,[11] and has been shown to add chlorine directly,[12] but it does not add bromine, and attempts to prepare tetraphenyldibromethane have led to tetraphenylethylene itself.[13]

[8] We are indebted to Professor G. E. K. Branch and to Dr. G. W. Wheland for pointing this out to us.

[9] L. Pauling and J. Sherman, J. Chem. Phys. **1**, 606 (1933); L. Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).

[10] The values of ΔH for addition to a non-conjugated double bond are 1.08 v.e. less than these, so that such addition reactions are all exothermic.

[11] W. H. Zartman and H. Adkins, J. Am. Chem. Soc. **54**, 1668 (1932).

[12] H. Finkelstein, Ber. Dtsch. Chem. Ges. **43**, 1533 (1910); J. F. Norris, R. Thomas and B. M. Brown, ibid. **43**, 2940 (1910). See also J. Schmidlin and R. v. Escher, ibid. **43**, 1153 (1910). The resultant dichlortetraphenylethane decomposes easily, mainly with the liberation of HCl and the formation of tetraphenylethylene with Cl substituted in the para position in one of the phenyl groups.

[13] H. Biltz, Ann. d. Chemie **296**, 231 (1897). H. Finkelstein, reference 12.

The Virial and Molecular Structure

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The virial theorem can be applied to a molecule, assuming that external forces are applied to keep the nuclei fixed. The mean electronic kinetic energy is then the negative of the mean total internal energy, plus a term arising from the virial of the external force. Since the external force is derivable from the knowledge of the total internal energy as function of nuclear position, this theorem gives a means of finding kinetic and potential energy separately for all configurations of the nuclei, as soon as the total energy is known, from experiment or theory. By using simple forms of curve for total energy, for the diatomic molecule, the kinetic and potential energy are derived and discussed. The curves give direct indication of the formation of the covalent bond, in cases where this occurs, by describing the removal of charge from the atoms to the region between the atoms, with resulting decrease of kinetic energy, increase of potential energy.

THE study of molecular structure has been too much based on particular models, rather than on general principles. One such general principle which has not been used and yet which seems capable of shedding considerable light on molecular problems, is the virial theorem. It is known that this theorem holds in quantum as in classical mechanics (see the Appendix for a simple proof) and its application to the theorem that the kinetic energy of an atom is the negative of the total energy is familiar. We shall use it, however, in a rather different way, applying it in the case where there are impressed forces.

THE VIRIAL THEOREM WITH IMPRESSED FORCES

The familiar statement of the virial theorem is

$$\overline{\text{K.E.}} = -\tfrac{1}{2}\overline{(xF_x+yF_y+\cdots)},$$

where the term on the right is a summation over all coordinates of the system, and F_x represents the force acting on the x coordinate, etc. We apply the theorem to a molecule consisting of electrons and nuclei attracting and repelling according to the inverse square law. Then, by a familiar argument, the virial $\overline{(xF_x+\cdots)}$ of the inverse square forces equals the potential energy of those forces, so that if the system is left to itself, the mean kinetic energy is minus half of the mean potential energy. But we shall not leave the system to itself. We shall rather assume that external forces of constraint act on the nuclei, just sufficient to keep the nuclei at rest, instead of allowing them to vibrate as they would if they were free. In applying the virial theorem, we shall now have to compute merely the electronic kinetic energy, since there is no nuclear kinetic energy of vibration. The part of the virial coming from the inverse square forces will be, as usual, equal to the potential energy of these forces. But, in addition, there will be a contribution to the virial coming from the external forces of constraint. Thus the kinetic energy will, on the average, be different from minus a half of the mean potential energy. It will be equal to this quantity only in two cases: at infinite separation of all atoms from each other and at the equilibrium configuration, in which the atoms could exist without vibration at the absolute zero. For, in both these cases, the atoms would remain in equilibrium without external forces of constraint, these forces would have no virial and only the virial of the inverse square forces need be considered. This is true only to the extent to which we can neglect zero point vibration; it seems that the arguments of the present paper are all accurate only to that approximation, since it is not exactly legitimate to replace the coupling between electronic and nuclear motion by an external force acting on the nuclei.

To fix our attention on a definite problem, we shall consider a diatomic molecule, though the results we shall obtain can easily be generalized to any molecule or solid. Let the impressed force

on nucleus 1 be F_1, on nucleus 2 F_2, where $F_2 = -F_1$, to keep the molecule as a whole in equilibrium. Then

$$\overline{(xF_x+\cdots)} = \overline{(r_1\cdot F_1+r_2\cdot F_2)} = \overline{(r_2-r_1)\cdot F_2}.$$

The vector r_2-r_1 is simply the vector from the first nucleus to the second. Since F_2 is parallel to this vector, with a diatomic molecule, the result is $\overline{rF}$, where r is the internuclear distance, F the force to hold the nuclei in equilibrium. If the nuclei are attracting each other, this force is outward and the product is positive, while if they are repelling it is negative. Thus for a diatomic molecule in an attractive region, the mean kinetic energy is less than minus half the mean potential energy of the electrostatic forces, while in a repulsive region it is greater.

The Kinetic Energy of a Diatomic Molecule

Again, confining ourselves to the simple case of the diatomic molecule, we can easily see that the results of the last section allow an unambiguous determination of the mean electronic kinetic energy of the molecule as a function of internuclear distance, as soon as the curve of total electronic energy as function of distance (the familiar "potential energy curve" of the molecule) is known. Let this electronic energy, the sum of the electronic kinetic and potential energy $(T+V)$ be called E. Then the force exerted by the nucleus 2 is $-dE/dr$ and the force F which equilibrates this is dE/dr. Hence we have, dropping the average signs for convenience,

$$T = -\tfrac{1}{2}V - \tfrac{1}{2}r(dE/dr).$$

Solving this simultaneously with the equation $T+V=E$, we have

$$T = -E - r(dE/dr), \quad V = 2E + r(dE/dr).$$

These important equations determine the mean kinetic and potential energies as functions of r, one might almost say, experimentally, directly from the curves for E as function of r which can be found from band spectra. The theory is so simple and direct that one can accept the results without question, remembering only the limitation of accuracy mentioned above. Any model of molecular structure which permits the calculation of E will also permit the calculation of T and V directly from the model, without use of the virial theorem. These virial equations, then, will provide a valuable and independent check of the correctness of the wave functions of the model. This check in general is much more sensitive than that obtained from an approximately correct energy. For it is well known that the energy is stationary with respect to a slight variation of the wave function, so that almost the correct energy will be found from a poor wave function, whereas the relation between kinetic and potential energy changes rapidly for even small changes in wave function.

Kinetic and Potential Energy in Typical Cases

First we consider an attractive state of a molecule. At distances greater than the equilibrium distance, T is less than $-E$, going through a minimum in general, rising again, and equalling $-E$ at equilibrium. It is rising rapidly with decreasing distance at equilibrium. It does not continue to rise indefinitely, however. For as the nuclei of the two atoms are pushed into coincidence, the atoms coalesce into a single atom whose atomic number is the sum of the atomic numbers of the two atoms and, of course, this combined atom has a finite kinetic energy. This is in agreement with the result of the virial theorem. For, at very small distances, the total energy E will be the sum of two terms: the repulsion $Z_1Z_2e^2/r$ of the two nuclei of atomic numbers Z_1 and Z_2, and the energy E' of the electrons of the combined atom. Thus for very small r's, we have

$$T = -(E'+Z_1Z_2e^2/r) - r(d/dr)(E'+Z_1Z_2e^2/r) = -E',$$

$$V = 2(E'+Z_1Z_2e^2/r)+r(d/dr)(E'+Z_1Z_2e^2/r) = 2E'+Z_1Z_2e^2/r.$$

That is, the kinetic energy of the electrons is the negative of the total energy of the combined atom, a finite amount, while the potential energy is the sum of twice the total energy of the combined atom and the nuclear repulsion, all just as we should expect. For a repulsive state the situation is similar except that the preliminary

decrease of kinetic energy at large r is not present.

These results become more definite if we take some of the well-known approximate formulas for interatomic energy and compute kinetic and potential energy from them. We should state at the outset that no one of these formulas has the correct behavior at $r=0$. Hence we can expect a reasonable behavior only in the neighborhood of the equilibrium distance and for larger distances. First we take the power series formula used by Born and others for crystal structure. This gives

$$E=E_\infty-a/r^n+b/r^m,$$

$$T=-E_\infty-(n-1)a/r^n+(m-1)b/r^m,$$

$$V=2E_\infty+(n-2)a/r^n-(m-2)b/r^m,$$

where E_∞ is the energy at infinite separation. Assuming that $m>n$, and that both m and n are greater than unity, we see that the kinetic energy first decreases with decreasing r, as we have stated, then goes through a minimum similar to that of the total energy, rising again and becoming infinite as $r=0$. The minimum of kinetic energy is easily shown to be at a larger r than the equilibrium distance, by a factor $\{(m-1)/(n-1)\}^{1/(m-n)}$, which, for example, is about 1.2 in the typical case $m=9$, $n=5$. Similarly, V rises for large r, goes through a maximum at a slightly larger r than the minimum of the kinetic energy, then decreases without limit. This, of course, neglects the fact which we have pointed out, that at still smaller distances the potential energy goes through a minimum and again increases, becoming positively infinite as r approaches zero. In Fig. 1 we show curves for E, T and V, for the case $m=9$, $n=5$. The case $n=1$, where the attractive forces are electrostatic, as in an ionic crystal or molecule, is exceptional. For in that case the second term in T, involving the factor $n-1$, is zero. The kinetic energy then does not go through its initial dip but begins to increase immediately as r decreases, going up with the same power of $1/r$ as the repulsive potential. The term $-a/r$, appearing in E, comes, in this case, entirely from the potential energy.

A purely repulsive state can be approximated, in terms of inverse powers, by a single term

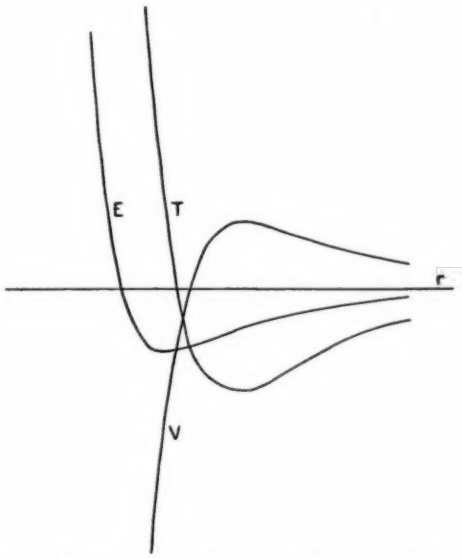

FIG. 1. Kinetic, potential and total energy of diatomic molecule as function of r. Energy is assumed to be of form $-a/r^6+b/r^9$.

b/r^m, obtained in the formulas above by setting $a=0$. Here we see that the kinetic energy increases, and the potential energy decreases, with decreasing r, according to the same inverse power as the total energy. In this case again, the behavior for very small r is not correctly given. One interesting feature, which is met also in the attractive case, is that if m is large, the kinetic and potential energies separately are much larger than the total energy, which appears as the small difference of two large quantities.

The features of which we have spoken are not peculiar to the particular energy formula which we have used. If the energy is approximated by a sum of two exponential terms, as in the Morse curve, or in a repulsive case by a single exponential, the behavior in the neighborhood of the minimum and for large r is essentially similar to what we have described. The formulas are easily derived and it is hardly necessary to discuss them in detail.

INTERPRETATION OF KINETIC AND POTENTIAL ENERGY CURVES

The curves for kinetic and potential energy which we have discussed in the preceding section and plotted in Fig. 1, seem at first sight to be unexpected. We consider first the attractive case,

taking homopolar valence, for which n would be about 5 (or for which we would use a Morse curve, which gives results like Fig. 1). For we see that the decrease of energy which is responsible for binding seems to come from a decrease of kinetic energy, rather than of potential energy. The theory of homopolar binding suggests, on the other hand, that the mechanism of this binding is one in which charge concentrates between the nuclei and is attracted electrostatically by both nuclei, this attraction producing the binding. Thus we should expect that the binding would result from a decrease in potential energy, rather than kinetic. The answer to this paradox is not far to seek, however. We have just said that the first step in homopolar binding is the concentration of charge in the region between the nuclei. Now it requires a relatively small amount of energy (as we can see from the minimum principle for energy) to pull a certain amount of charge from the inner part of the atom, where it is ordinarily found, out to the periphery, as for example the region between the atoms. It can very well be that the decrease of potential energy made possible by this change, coming from the attraction of the electron of one atom by the nucleus of the other, can decrease the total energy enough to make this the stable configuration and produce binding. But when the charge is pulled out to the edge of the atom, its potential energy increases greatly, as it is separated from the nucleus, and its kinetic energy correspondingly decreases. Thus the rise of potential energy and the fall of kinetic energy, noticed in Fig. 1, are produced. As the atoms are pushed further together, however, a point is reached where the charge to be shared is fully removed to the region between the atoms. Further decrease of r then produces no further removal of charge to the periphery, no further decrease of kinetic and increase of potential energy. Instead, the other, more fundamental influences come into play. The kinetic energy begins to rise as the electrons are forced into smaller space. This may be likened to the adiabatic rise of energy of an electron gas compressed in a box. And the potential energy falls, as the negative charge concentrated between the atoms and the positive charge left over on the atoms come closer together. The attractive force of the electrical attractions balances the repulsion of the electronic motion at equilibrium, the positive slope of the potential energy curve indicating large attraction, and the negative slope of the kinetic energy large repulsion. The curves show, then, that in the neighborhood of the equilibrium position, and even more at smaller distances, the behavior of the valence bond is rather simple and quite as we should expect. The peculiar behavior of potential and kinetic energies at larger r can be definitely associated with the formation of the shared electron pair which is responsible for the bond. This interpretation can be made rather unambiguously without use of models; for it is hard to see any meaning which can be given to an increase in electronic potential energy, decrease in kinetic, with much smaller change in total energy, other than a shift of electrons toward the outside of the atom.

Our identification of the minima and maxima, respectively, of the kinetic and potential energy for large r with the formation of a shared electron pair becomes much more reasonable when we consider the other cases of energy curves. We have already seen that these minima and maxima do not occur in the case where the attractive force is electrostatic, as in ionic molecules ($n=1$), or in repulsive molecular states. In both these cases, the usual theory is that no electron pair is formed. The only action is the electronic repulsion when the atoms come closer together and, in the ionic case, the electrostatic attraction. This fits in perfectly with the behavior of the kinetic energy which rises rapidly, as the repulsive part of the energy does, at small distances.

The considerations which we have suggested indicate the importance of the virial in discussing molecular structure. There has been no attempt in this paper to deal exhaustively with its importance but only to point it out as a method which should be used in future work. And it should be recalled that it is as useful in treating more complicated molecules and solids, as with diatomic molecules. With a solid, for instance, if we subject it to a hydrostatic pressure p, the theorem becomes $T=-E+3pv$, if the internal forces are electrostatic, as is well known. Thus, here, the kinetic energy is greater than $-E$ for

positive pressures, less for negative pressures and, in general, shows just the sort of behavior as function of volume that we have discussed for diatomic molecules as a function of r. The same conclusions regarding the nature of the interatomic forces can be drawn here as for molecules. Such conclusions were drawn before the wave mechanics by Schottky,[1] but his paper seems to have had but small influence in the theory of solids.

Appendix

Let Schrödinger's equation be

$$\sum_i -\frac{h^2}{8\pi^2 m_i}\frac{\partial^2\psi}{\partial x_i^2}+(V-E)\psi=0.$$

We differentiate with respect to x_j, and multiply by $x_j\bar{\psi}$, obtaining

$$\sum_i -\frac{h^2}{8\pi^2 m_i}x_j\bar{\psi}\frac{\partial^3\psi}{\partial x_i^2\partial x_j}+\left(x_j\frac{\partial V}{\partial x_j}\right)\bar{\psi}\psi+x_j(V-E)\bar{\psi}\frac{\partial\psi}{\partial x_j}=0.$$

Now by Schrödinger's equation for $\bar{\psi}$, the last term is equal to

$$\sum_i \frac{h^2}{8\pi^2 m_i}x_j\frac{\partial^2\bar{\psi}}{\partial x_i^2}\frac{\partial\psi}{\partial x_j}.$$

We substitute this term in and sum over x_j, obtaining

$$\sum_i -\frac{h^2}{8\pi^2 m_i}\sum_j\left[x_j\left(\bar{\psi}\frac{\partial^3\psi}{\partial x_i^2\partial x_j}-\frac{\partial^2\bar{\psi}}{\partial x_i^2}\frac{\partial\psi}{\partial x_j}\right)\right]+\left(\sum_j x_j\frac{\partial V}{\partial x_j}\right)\bar{\psi}\psi=0.$$

We now integrate this equation over the coordinate space. In doing this, we integrate the first term by parts. We do this by means of the identity

$$\sum_j x_j\left(\bar{\psi}\frac{\partial^3\psi}{\partial x_i^2\partial x_j}-\frac{\partial^2\bar{\psi}}{\partial x_i^2}\frac{\partial\psi}{\partial x_j}\right)=-2\bar{\psi}\frac{\partial^2\psi}{\partial x_i^2}+\frac{\partial}{\partial x_i}\left[\bar{\psi}^2\frac{\partial}{\partial x_i}\left(\frac{\sum_j x_j(\partial\psi/\partial x_j)}{\bar{\psi}}\right)\right],$$

which can be proved, after a little manipulation, by performing the differentiations indicated on the right. In integrating the right side of this over the coordinates, the derivative integrates to zero if we assume the system to be a closed one, for then we take the limits of integration at infinity, where $\psi=0$. Hence we are left with only

$$\sum_i -\frac{h^2}{8\pi^2 m_i}\int\bar{\psi}\frac{\partial^2\psi}{\partial x_i^2}\,d\tau=-\tfrac{1}{2}\int\sum_j x_j\left(\frac{-\partial V}{\partial x_j}\right)\bar{\psi}\psi\,d\tau.$$

The left side is recognized as the mean kinetic energy, the right side as $-\frac{1}{2}$ times the mean of $\sum_j x_j(-\partial V/\partial x_j)$, which is just the virial, when we remember that $F_j=-\partial V/\partial x_j$.

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[1] Schottky, Phys. Zeits. **21**, 232 (1920).

The Free Energy, Entropy and Heat Capacity of Bromine and of Hydrogen Bromide from Spectroscopic Data

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The free energy, entropy and heat capacity of gaseous bromine and of hydrogen bromide have been computed for the temperature range 200–1600°K. The equilibrium constants for the reaction $Br_2 = 2\,Br$, obtained from these numbers and the spectroscopic heat of dissociation, differ from Bodenstein's values by more than his apparent experimental error. Calculations for the dissociation of hydrogen bromide give results which agree with the e.m.f. measurements of Bodenstein and Geiger, but are in definite disagreement with the experiments of von Falckenstein when the latter are corrected for the dissociation of bromine.

IN A recent paper,[1] Brown, who had effected the rotational analysis of the bromine spectrum,[2] reported that a calculation of the equilibrium constant for the dissociation of diatomic into monatomic bromine "by the Gibson and Heitler equation" leads to values of log K which were uniformly about 0.15 less than the experimental results of Bodenstein.[3] This discrepancy was so surprising in view of the excellent agreement found by Gibson and Heitler[4] in the case of the iodine dissociation that it seemed worth while to recompute the equilibrium. Brown gave no details of his calculation, but presumably treated the rotational-vibrational levels of the bromine molecule as those of a rigid rotator combined with a harmonic oscillator; it did not seem likely that the error introduced by this simplification could account for the serious discrepancy (0.7 cal./deg. in $R \ln K$) which he reported, but we have nevertheless computed the free energy, entropy and heat capacity for the temperature range 200–1600°K, taking account of the interaction and stretching terms in the formula for the energy levels. Since the dissociation of hydrogen bromide into hydrogen and bromine has been measured by von Falckenstein,[5] we have also carried out similar calculations for hydrogen bromide.

Brown[2] gives for $Br^{79}-Br^{81}$, $\epsilon_v = 323.2(v+\frac{1}{2}) - 1.07(v+\frac{1}{2})^2$, $B_v = 0.08077 - 0.000275v$, $D = -2.03\times10^{-8}$. Owing to the existence of the two isotopes of bromine in almost equal proportions (0.505 : 0.495), the three diatomic varieties will exist at high temperatures in the proportions 0.255 of 79–79, 0.500 of 79–81, 0.245 of 81–81. As far as the calculation of thermodynamic reaction quantities is concerned, it has been shown[6] that it is permissible to calculate the free energy and entropy as if the substance were non-isotopic, provided that this procedure is adopted for each of the reactants and products, and that the spectroscopic constants used in the computation are averages, the result of properly weighting the constants for each of the isotopic varieties. Calculation shows that such effective constants for bromine are (within the limits of experimental error) just those for 79–81 and the calculation can thus be carried out with these constants as if for a non-isotopic bromine of molecular weight 159.83; it is necessary, of course, to add the usual symmetry correction for a homonuclear diatomic molecule, $-R \ln 2$, in spite of the fact that all rotational levels are present in 79–81 with full statistical weight.

The free energy, entropy and heat capacity entered in Table I[7] were obtained from Gordon

[1] W. G. Brown, J. Am. Chem. Soc. **54**, 2394 (1932).
[2] W. G. Brown, Phys. Rev. **39**, 777 (1932).
[3] Bodenstein, Zeits. f. Elektrochemie **22**, 327 (1916).
[4] Gibson and Heitler, Zeits. f. Physik **49**, 465 (1928).
[5] von Falckenstein, Zeits. f. physik. Chemie **68**, 270 (1909).
[6] Giauque and Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932); see also Gordon and Barnes, J. Phys. Chem. **36**, 2292 (1932) and reference 1.
[7] In the calculations, the values of the universal constants are those given in Int. Crit. Tab., Vol. I.

and Barnes,[8] Eqs. (6), (9) and (11). For temperatures less than 700°K, the quantities ($\ln Q_v + \epsilon_0 hc/kT$), S_v/R, C_v/R, $\bar{v}$, $\bar{v}^2$, s_1, s_2, c_1, c_2 were obtained by interpolation in their Tables I–XI; for temperatures $\gtrsim$700°K, $\omega_e hc/kT$ lies beyond the range of the tables and therefore the calculation was carried out as shown in their Example 4, the integrations starting from $v=11$, as in that example. There is an additional small correction that contributes to the heat capacity at the highest temperatures but not to the entropy or free energy; this is due to the excited electronic states[9] 14,734 and 15,891 cm^{-1} above the normal $^1\Sigma$ state of the molecule. The first of these excited states is unclassified and no correction can be applied as yet but the second is presumably $^3\Pi$ with $\epsilon_v' = 169.7(v'+\frac{1}{2}) - 1.913(v'+\frac{1}{2})^2$ and $B' = 0.0592$. To a good enough approximation, the resulting contribution to the heat capacity is given by

$$6R \cdot \left(\frac{Ahc}{kT}\right)^2 \cdot e^{-Ahc/kT} \cdot \left[\frac{B_0}{B_0'} \cdot \frac{\Sigma e^{-\epsilon_v' hc/kT}}{\Sigma e^{-\epsilon_v hc/kT}}\right]$$

where $A = 15{,}891$. The numerical value of this term is only 0.004 for 1600° and 0.002 for 1500° and is included in the numbers entered in Table I.

In the case of hydrogen bromide, the constants[10] are $\epsilon_v = 2647(v+\frac{1}{2}) - 44(v+\frac{1}{2})^2$, $B_v = 8.342 - 0.225v$, $D = -0.000{,}325$, and the quantities necessary for the calculation can be obtained for the whole temperature range from the tables. The effect of the H^2 isotope of hydrogen on the effective spectroscopic constants has been ignored, since this is vanishingly small[11] except for artificially enriched samples.

None of the values of $-(F°-E_0°)/T$ and $S°$ in Table I includes the nuclear spin contribution. For bromine (since $j_e = 3/2$) this would amount to R ln 16 and must be added to the entries, as must the isotope contribution, if "absolute" values are desired; for hydrogen bromide, the spin contribution would be R ln 8.

[8] Gordon and Barnes, J. Chem. Phys. **1**, 297 (1933).

[9] W. G. Brown, Phys. Rev. **38**, 1179 (1931), also reference 2; Weizel, *Bandenspektren*, p. 385, Leipzig (1931).

[10] Czerny, Zeits. f. Physik **44**, 235 (1927); Kratzer, Zeits. f. Physik **3**, 289 (1920); Weizel, *Bandenspektren*, p. 327.

[11] Urey and Rittenberg, J. Chem. Phys. **1**, 137 (1933).

TABLE I.

	Bromine			*Hydrogen Bromide*		
T°K	$-(F°-E_0°)/T$	$S°$	$C_P°$	$-(F°-E_0°)/T$	$S°$	$C_P°$
200	47.822	55.291	8.272	37.786	44.703	6.959
250	49.509	57.162	8.486	39.330	46.256	6.961
298.1	50.868	58.667	8.618	40.550	47.481	6.964
300	50.918	58.722	8.622	40.594	47.526	6.964
350	52.130	60.058	8.713	41.663	48.599	6.970
400	53.196	61.226	8.777	42.589	49.530	6.983
450	54.146	62.263	8.824	43.407	50.354	7.006
500	55.006	63.194	8.859	44.139	51.094	7.039
550	55.789	64.040	8.888	44.802	51.767	7.085
600	56.509	64.814	8.911	45.409	52.386	7.141
650	57.176	65.528	8.931	45.968	52.960	7.204
700	57.797	66.191	8.948	46.487	53.496	7.274
750	58.377	66.809	8.963	46.971	54.001	7.350
800	58.922	67.388	8.977	47.426	54.477	7.426
850	59.437	67.932	8.989	47.854	54.930	7.503
900	59.923	68.446	9.001	48.259	55.361	7.580
950	60.384	68.933	9.011	48.644	55.773	7.656
1000	60.823	69.396	9.022	49.010	56.168	7.730
1050	61.242	69.836	9.031	49.360	56.547	7.801
1100	61.643	70.257	9.041	49.695	56.911	7.869
1150	62.026	70.659	9.050	50.016	57.263	7.934
1200	62.394	71.044	9.059	50.325	57.602	7.996
1250	62.747	71.414	9.068	50.623	57.929	8.055
1300	63.087	71.770	9.077	50.911	58.247	8.111
1400	63.732	72.443	9.094	51.456	58.851	8.214
1500	64.334	73.071	9.113	51.969	59.421	8.307
1600	64.898	73.660	9.132	52.451	59.960	8.390

It is, perhaps, of interest to note what error would have been introduced in Table I if the second order terms in the energy level formula had been ignored. If, for 1600°K, bromine had been treated as a harmonic oscillator of frequency $\omega_e(1-2x) = 321.1$ plus a rigid rotator ($B = 0.080{,}77$), the entries[12] in Table I would have been 64.826, 73.494 and 8.927. In the case of $-(F°-E_0°)/T$, neglect of the anharmonic term in x causes an error of 0.036 in the final result, neglect of the interaction terms which take account of the change in B with v, an error of 0.022 and neglect of the stretching terms involving D, an error of 0.014. In the case of the heat capacity at the same temperature, the corresponding errors are 0.112, 0.060 and 0.030, respectively, which (with the contribution 0.004 from the excited $^3\Pi$ state) just account for the difference between the value 8.927 and the entry in the table. In the case of hydrogen bromide at

[12] Using the notation of reference 8 for bromine at 1600°K, we find that $(\ln Q_v + \epsilon_0 hc/kT) = 1.4055$, $S_v/R = 2.2941$, $C_v/R = 1.0493$, $\bar{v} = 3.16$, $\bar{v}^2 = 23.9$, $s_1 = 6.98$, $s_2 = 78.9$, $c_1 = 8.20$, $c_2 = 186$; $\beta_1 = 0.003{,}405$, $\beta_2 = 1.16 \times 10^{-5}$, $\bar{d} = d_0(1 + 0.0068\bar{v}) = 0.00709$.

1600°, the assumption that its spectrum could be treated as that of a harmonic oscillator of frequency 2559 plus a rigid rotator with $B = 8.342$, would lead to the values 52.418, 59.884 and 8.260 instead of the numbers entered in the table.

The Thermal Dissociation of Bromine

From Brown's value of the heat of dissociation,[9] 1.962 volts, $\Delta E_0°$ for the reaction $Br_2 = 2\,Br$ is 45,230 cal. The values of $-(F°-E_0°)/T$ for monatomic bromine can be readily computed since the "State Sum" for monatomic bromine is simply $(4+2\cdot\exp[-3685hc/kT])$ where 3685 cm^{-1} is the separation[13] of the $^2P_{\frac{1}{2}}$ and $^2P_{\frac{3}{2}}$ states of the bromine atom. The resulting $-R \ln K_1 = R \ln (P_{Br_2})/(P_{Br})^2$ are entered in Table II and correspond to the continuous curve of Fig. 1; the figure also shows the experimental results of Bodenstein[3] and of Perman and Atkinson[14] as recalculated by Lewis and Randall.[15] It is evident that there is still a difference of about half a calorie per degree between Bodenstein's results and the entries in Table II, and that this discrepancy is considerably larger than his apparent experimental error. This result is rather surprising, since there is no reason to distrust the spectroscopic data and Bodenstein's figures give every internal evidence of self-consistency.

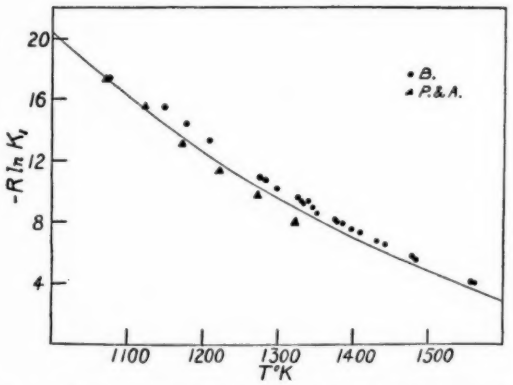

FIG. 1. The equilibrium constant for the thermal dissociation of bromine. $K_1 = (P_{Br})^2/(P_{Br_2})$.

Table II. $K_1 = (P_{Br})^2/(P_{Br_2})$ *and* $K_2 = (P_{HBr})/(P_{H_2})^{\frac{1}{2}} \cdot (P_{Br_2})^{\frac{1}{2}}$.

	$Br_2(g) = 2Br$		$\frac{1}{2}H_2 + \frac{1}{2}Br_2(g) = HBr(g)$	
T°K	$-R \ln K_1$	$\Delta F°$ kcal.	$R \ln K_2$	$-\Delta F°$ kcal.
298.1	128.92	38.43	43.12	12.85
300	127.95	38.39	42.86	12.86
350	106.09	37.13	37.09	12.98
400	89.68	35.87	32.75	13.10
450	76.89	34.60	29.36	13.21
500	66.65	33.33	26.63	13.32
550	58.26	32.04	24.40	13.42
600	51.26	30.76	22.53	13.52
650	45.33	29.47	20.94	13.61
700	40.25	28.17	19.58	13.70
750	35.83	26.87	18.39	13.79
800	31.96	25.57	17.35	13.88
850	28.55	24.27	16.43	13.97
900	25.51	22.96	15.61	14.05
950	22.78	21.64	14.88	14.13
1000	20.33	20.33	14.21	14.21
1050	18.11	19.02	13.61	14.29
1100	16.09	17.70	13.06	14.37
1150	14.24	16.38	12.57	14.45
1200	12.54	15.05	12.11	14.53
1250	10.97	13.72	11.68	14.61
1300	9.53	12.39	11.30	14.68
1400	6.94	9.72	10.60	14.84
1500	4.69	7.04	9.99	14.99
1600	2.71	4.34	9.46	15.14

From the entries of Table I, Giauque's data for hydrogen[16] and the calorimetrically determined heat of formation of gaseous hydrogen bromide, *viz.*, 12,100 cal., it follows that $\Delta F°_{298.1}$ for the reaction $\frac{1}{2}H_2 + \frac{1}{2}Br_2(g) = HBr(g)$ is $-12{,}850$ cal. and that $\Delta E_0°$ is $-11{,}990$ cal.[17] The resulting values of $R \ln K_2 = R \ln (P_{HBr})/(P_{H_2})^{\frac{1}{2}} \cdot (P_{Br_2})^{\frac{1}{2}}$ and of $\Delta F°$ for the reaction are given in Table II; these numbers agree with those given by Nernst's free energy equation[18] (which was based on the e.m.f. measurements of Bodenstein and Geiger)[19] within about a quarter of a calorie per degree in $R \ln K_2$ up to 1500°K.

The Dissociation of Hydrogen Bromide

Direct measurements on this equilibrium have been carried out by von Falckenstein,[5] the partial pressure of the hydrogen in the equilib-

[13] Turner, Phys. Rev. **27**, 397 (1926).

[14] Perman and Atkinson, Zeits. f. physik. Chemie **33**, 215, 577 (1900).

[15] Lewis and Randall, *Thermodynamics*, p. 514 (1923).

[16] Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).

[17] Datta, Zeits. f. Physik **77**, 404 (1932), gives 87,700 as the heat of dissociation of hydrogen bromide from measurements on continuous absorption. Combining this value with the heat of dissociation of hydrogen (102,900 cal., according to Richardson, Proc. Roy. Soc. **A123**, 466 (1929)) and of bromine, $\Delta E_0°$ is $-13{,}600$ cal. Datta's value, however, is based on a considerable extrapolation.

[18] Nernst, Zeits. f. Elektrochemie **15**, 687 (1909).

[19] Bodenstein and Geiger, Zeits. f. physik. Chemie **49**, 70 (1904).

rium mixture being determined by means of a semi-permeable platinum diaphragm. He found, as mean values for the forward and reverse reaction, P_{H_2} to be 1.91, 2.78 and 4.17 mm at 1297°, 1381° and 1495°, respectively,[20] with total pressures of 761, 764 and 777 mm. For these three temperatures, $1/K_1$ is 126, 41.5 and 11.2 from Table II, so that P_{Br_2} is 0.807, 0.830 and 0.707 mm and P_{HBr} is 756, 756 and 765 mm. The resulting $R \ln K_2$ for the three temperatures are 12.74, 12.34 and 12.11, respectively, in definite disagreement with the values found by interpolation from Table II, *viz.*, 11.32, 10.72 and 10.02. Thus the supposed agreement between von Falckenstein's results and those of Bodenstein and Geiger comes solely from the fact that the calculations based on von Falckenstein's measurements ignored the dissociation of diatomic into monatomic bromine. It should be noted in passing that Giauque and Overstreet[6] found a similar disagreement in the case of Löwenstein's measurements[21] on the dissociation of hydrogen chloride. The entries in Table II are of course uncertain to the extent of the error in the calorimetrically determined heat of formation of hydrogen bromide but von Falckenstein's $R \ln K_2$, after correction for the bromine dissociation, cannot be made self-consistent by any adjustment in the heat of formation.

[20] The dissociation of diatomic into monatomic hydrogen is negligible at these temperatures; see reference 16.

[21] Löwenstein, Zeits. f. physik. Chemie **54**, 715 (1906).

The Reactions of the Hydroxyl Radical in the Electrodeless Discharge in Water Vapor

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In a study of the reactions occurring in the electrodeless discharge in water vapor consistently high yields of hydrogen peroxide were obtained. A number of reactions have been studied and by a process of elimination a mechanism for the formation of hydrogen peroxide from hydroxyl has been suggested. In the course of some spectrographic investigations of the electrodeless discharge in water vapor some new bands, with heads at 3564 and 3328A, were observed which are probably due to an ionized hydroxyl. These bands were not present in the uncondensed electrode discharge but appeared in the condensed electrode discharge at low pressures.

WHEN a discharge is passed through water vapor the so-called "water" bands are excited. These bands are known to be due to the hydroxyl radical and it is supposed that an electron, having an energy of about nine volts, dissociates a water molecule into a hydrogen and an excited hydroxyl, which then emits the characteristic radiation,

$$HOH = H + OH. \qquad (1)$$

Even with the weakest discharge the hydroxyl bands are emitted with a surprising intensity. This would indicate the possibility of obtaining a high concentration of hydroxyl and numerous attempts have been made to study the reactions of this molecule. In this laboratory an attempt was made to obtain a molecular beam of hydroxyl but the attempt failed because no chemical reaction characteristic of hydroxyl was discovered and it was therefore uncertain as to whether hydroxyl itself were present in the beam. Abroad, Steiner[1] and Bonhoeffer[2] made similar attempts to study the chemical behavior of hydroxyl, likewise with negative results. Finally Bonhoeffer and Pearson[2] published an account of an unsuccessful attempt to obtain the hydroxyl bands in absorption. They reached the conclusion that the hydroxyl concentration was extremely low because of the rapid disappearance of hydroxyl by the reaction,

$$OH + OH = H_2O + O. \qquad (2)$$

It occurred to us that if this reaction takes place, a high concentration of atomic oxygen should be present in the vapor which has passed through the discharge and it should therefore be possible to obtain a molecular beam of atomic oxygen which could be identified by well-known methods.[3] In carrying out this result however we discovered that there was very little oxygen, either atomic or molecular, present in the discharge and that large yields of hydrogen peroxide were obtained, whereas Bonhoeffer and Pearson had reported only traces of hydrogen peroxide to be formed. This made it appear doubtful that reaction (2) was occurring and made necessary a careful study of the reactions actually taking place in the water vapor discharge.

EXPERIMENTAL

In the study of the chemical reactions the electrodeless discharge was used. The apparatus by which the discharge was produced was essentially the same as that described in a previous article.[4] A flow system was used in all the experiments. The water reservoir was made from 5 mm Pyrex tubing which had previously been calibrated so that the amount of water used during a run could be measured. The height of the water column was followed with a cathetometer. The

[1] Steiner and Bay, Zeits. f. physik. Chemie **3B**, 149 (1929).

[2] Bonhoeffer and Pearson, Zeits. f. physik. Chemie **14B**, 2 (1931).

[3] Kurt and Phipps, Phys. Rev. **34**, 1357 (1929).

[4] Rodebush and Klingelhoefer, J. Am. Chem. Soc. **55**, 130 (1933).

flow of water vapor was regulated by a capillary leak and by the temperature of the bath surrounding the reservoir. Conductivity water was always used in the reservoir.

The discharge was produced in a 200-cc Pyrex flask. Optimum conditions for high yields of hydrogen peroxide were at pressures of 0.1 to 0.2 mm of mercury. Under best conditions the discharge had a vivid red appearance, but if the discharge was too intense blue rings appeared, which followed the turns of the coil, indicating the presence of oxygen atoms. This was confirmed by spectrographic evidence. A better yield of hydrogen peroxide was obtained when the discharge bulb was cooled by a blast of air.

It was found expedient to use a U-tube trap for collecting the sample. In the early course of the work ground glass joint traps, which necessitate the use of stopcock grease, were employed and it was found impossible to obtain consistently large yields of hydrogen peroxide. A second U-tube trap was placed in series with the first to determine if all the sample was caught in the first trap. Two runs indicated that no condensable products escaped through the first trap.

After a run had proceeded the desired length of time and the sample frozen out in the liquid air-cooled trap, the apparatus was shut off from the pumps by a large stopcock. The vacuum was broken, drawing the air slowly through a liquid air trap so no moisture would be carried into the trap containing the sample. When the pressure within the apparatus was atmospheric the sample was permitted to melt. The trap was then cut off, weighed, and the sample titrated with 0.1 N. potassium permanganate. After a thorough rinsing the trap was dried and reweighed. The sampling process was carried out as hurriedly as possible in order to minimize decomposition of peroxide. A set of representative data is given in Table I.

TABLE I.

Millimols water used	Mol % water converted to hydrogen peroxide and hydrogen	Mol % water converted to hydrogen and oxygen
1 18.67	50.5	4.9
2 18.50	50.8	4.6
3 18.77	48.8	2.0
4 20.30	58.2	2.6

Effect of surface

The reaction tube was filled with Pyrex tubing so that the surface-volume ratio was increased more than fivefold. There was no increase in yield of peroxide, showing that the peroxide forming reaction is not influenced by the surface of the confining vessel. Results are given in Table II.

TABLE II.

Surface volume (cm)	Time (min.)	Wt. sample (g)	Wt. H_2O_2 (g)	% H_2O_2 in sample
2.09	75	0.60	0.318	53.0
11.80	60	0.45	0.221	49.0

From time to time during the course of this work it was noticed that the peroxide yields were lowered whenever the glass became very warm. The reaction tube was placed in an ice bath and several runs made to determine if decomposition occurred when the wall was at room temperature. There was no variation in the yield of peroxide.

Effect of distance

A study was made of the yield of hydrogen peroxide as a function of the distance between the discharge bulb and the trap. The results are shown in Table III.

TABLE III.

Distance (cm)	Wt. % H_2O_2 in sample	Distance (cm)	Wt. % H_2O_2 in sample
160	50.2	17	50.0
100	50.7	3	52.0
40	51.6	3*	47.0

* This run was made with a very high rate of flow.

Action of catalysts

By the action of a silver screen catalyst, an attempt was made to destroy the active species at varying distances down the reaction tube and determine what effect it would have on the peroxide yields. As soon as the discharge was turned on the catalyst became hot and some metal evaporated to the walls of the tube, causing it also to be catalytically active. Analysis of the sample showed only a very small fraction of a percent of peroxide present. It seemed plausible

that, even if the peroxide were formed before it reached the catalyst, it would be decomposed by the hot metal. A concentrated solution of hydrogen peroxide (85 percent) was prepared by the method given by Rice, Reiff and Kilpatrick.[5] The vapor from this solution was passed through the apparatus, which was entirely free of any catalyst, and a sample collected and analyzed. This procedure was repeated with the catalyst in the reaction tube. The sample in the first case tested about 65 percent by weight of peroxide and in the latter only 3 percent, showing that practically a quantitative decomposition of peroxide was brought about by the catalyst. A chemically deposited silver mirror was found to be equally effective for the decomposition of peroxide.

Taylor and Lavin[6] found that dehydrogenation catalysts, such as zinc chromite, were selective for atomic hydrogen recombination but did not destroy the hydroxyl molecules. The discharge bulb and reaction tube were coated with a similar dehydrogenation catalyst, copper chromite, and a discharge run on water vapor. The collected sample showed no peroxide present.

It would be very desirable to know whether the hydrogen peroxide is formed in the vapor immediately after the latter leaves the discharge or only by condensation in the liquid air trap. A possible method for detecting hydrogen peroxide vapor is the photography of the ultraviolet absorption spectrum. The absorption spectrum of hydrogen peroxide vapor was found by Urey, Dawsey and Rice[7] to be continuous in the region from 2150 to 2750A. An attempt was made to obtain the absorption spectrum of peroxide as formed in the water vapor discharge. The discharge bulb was placed near a long absorption tube but arranged so the discharge would not be photographed. Quartz windows were sealed on each end of the absorption tube. A small hydrogen arc was used as a source of continuum and was found to give consistently reproducible intensities. Several plates were taken with the discharge in operation but no noticeable absorption was obtained. A blank run was made passing the vapor from a concentrated solution of peroxide through the absorption tube and several pictures were taken. A very small amount of absorption was indicated. The partial pressure of peroxide in these blank runs was about 10 times greater than that occurring in the water vapor discharge. It is evident that the partial pressure of peroxide as found in the water vapor discharge is too small to give any noticeable absorption.

Since it was not possible to determine either exactly where the hydrogen peroxide is formed or what the mechanism is by which it is formed there remained only the alternative of settling the mechanism by a process of elimination. Accordingly a number of chemical reactions which might produce hydrogen peroxide were tried out.

Condensation of oxygen atoms with water in the trap

Water vapor was rapidly drawn through the apparatus and frozen out in the trap, taking care to obtain a reasonably uniform layer of water on the walls of the trap. A discharge was then run with oxygen, at about 0.2 mm pressure, and a sample collected over a period of 60 minutes. The sample gave no reaction with potassium permanganate indicating the absence of hydrogen peroxide. It did have an ozone odor and colored a solution of potassium iodide. Three different trials indicated the same results.

The apparatus was changed so that the distance between the discharge bulb and the trap was about 1.6 meters. In traversing this distance the oxygen atoms would have completely disappeared, so that there would be no possibility of a reaction involving oxygen atoms in the trap. A run of some hours' duration was made with the water vapor discharge and a sample collected. Titration with permanganate showed the sample to be 50.2 percent by weight peroxide. The possibility of a condensation reaction in the trap involving oxygen atoms appears to be excluded.

Reaction of hydrogen atoms with oxygen

The oxygen was introduced into the active species from the hydrogen discharge a short distance from the discharge bulb, taking pre-

[5] Rice, Reiff and Kilpatrick, J. Am. Chem. Soc. **48**, 3019 (1926).

[6] Taylor and Lavin, J. Am. Chem. Soc. **52**, 1910 (1930).

[7] Urey, Dawsey and Rice, J. Am. Chem. Soc. **51**, 1371 (1929).

cautions to prevent back diffusion of the oxygen into the bulb. The spectrum of the discharge did not change on admittance of the oxygen into the reaction tube so it was assumed that back diffusion was negligible. The flow of gases was measured by gas burettes and regulated by capillary leaks. Results are shown in Table IV.

TABLE IV.

No.	Time (min.)	Flow of gas (cc./min. at atmos. conditions) H_2	O_2	Wt. sample (g)	Wt. H_2O_2 (g)	% H_2O_2 in sample
1	98	22.0	1.30	0.70	0.022	3.1
2	80	15.5	3.70	0.06	0.0002	0.33
3	110	6.3	1.15	0.06	0.039	64.5
4	60	14.0	1.10	0.05	0.020	40.0

At the higher rates of flow the yields were very noticeably decreased, but, the reaction tube in the region of the entrance of the oxygen became very warm. It was consistently observed in the course of this work that whenever the glass became heated the yield of peroxide was always decreased.

Reaction of oxygen atoms with hydrogen

Several trials were made, employing different rates of flow, but in no case was any appreciable amount of hydrogen peroxide present. Usually one to three drops of standard permanganate would give a pink coloration. Good yields of water were obtained and a small amount of ozone was noted. The heating effect in the reaction tube was quite small.

Reaction of oxygen atoms with water

Runs were made varying the pressure of oxygen in the discharge bulb and the rate of flow of water vapor but no trace of peroxide was found in any of the samples. Because of the small sample obtained runs of several hours duration were made. Small amounts of ozone were detected.

Reaction of hydrogen atoms with water

No evidence of any sort of a reaction was noticed. No peroxide was found in the samples and there was no heating effect at the entrance of the water vapor into the active species from the hydrogen discharge.

Reaction of the active species from the water vapor discharge and oxygen

A discharge was run on the water vapor and the oxygen added to the active species in the reaction tube. The results are given in Table V. The weight of the sample is larger than the amount of water used in each measurable case. Beside the reactions occurring in the water vapor discharge the reaction between hydrogen atoms and oxygen molecules occurs, and it was found to yield both peroxide and water.

TABLE V.

No.	Time (min.)	Wt. H_2O_2 used (g)	Flow O_2 (cc./min.)	Wt. sample (g)	Wt. % H_2O_2 in sample
1	90		0.83	0.160	53.1
2	90		2.20	0.160	47.2
3	45	0.372	1.13	0.410	55.3
4	60	0.532	1.13	0.588	55.0

Effect of premixing hydrogen and water vapor

The hydrogen was added to the water vapor before passing into the discharge bulb. Two trials were made and in each case the yield was about the same as in the water vapor discharge. (See Table VI.) This indicates that there is very little oxygen present with which the hydrogen may react.

TABLE VI.

Time (min.)	Flow of H_2 (cc./min.)	Wt. H_2O used (g)	Wt. sample (g)	Wt. H_2O_2 (g)	% H_2O_2 in sample
60	1.50		0.150	0.070	46.6
60	1.86	0.436	0.421	0.206	48.8

Effect of premixing oxygen and water vapor

Several runs were made and in each case the sample, which was larger than the amount of water used, tested about 50 percent peroxide. It appears that neither oxygen atoms nor mole-

TABLE VII.

No.	Time (min.)	Flow of O_2 (cc./min.)	Wt. H_2O used (g)	Wt. sample (g)	Wt. H_2O_2 (g)	% H_2O_2 in sample
1	40	2.30		0.12	0.059	49.7
2	45	1.34	0.336	0.362	0.164	45.3
3	40	0.715	0.337	0.350	0.187	51.6

cules participate in the peroxide forming reaction, for if they did the yield of peroxide should have been noticeably increased. (See Table VII.)

Spectrographic studies

The spectrum of the electrodeless discharge in water vapor was photographed with a Hilger quartz spectrograph (E38) with Eastman 40 plates. An exposure of a few seconds gave the well-known water bands at 3064 and 2811A and in addition some hitherto unreported bands. The strongest of these had a head at 3564A and was degraded toward the red. A fainter band had a head at 3328A. In order to ascertain if possible why these bands had not been previously observed the emission spectrum of water vapor was photographed in a Wood tube with aluminum electrodes. With a 60 cycle discharge no trace of the bands was obtained but with a condensed discharge the new bands came out very strongly at pressures in the neighborhood of 0.1 mm. At higher pressures they disappeared.

Several plates were made of the bands on a large spectrograph with a dispersion of 3A per mm. Preliminary assignments were made but the analysis proved to be very difficult and was not carried further.[8] The bands have a hydride

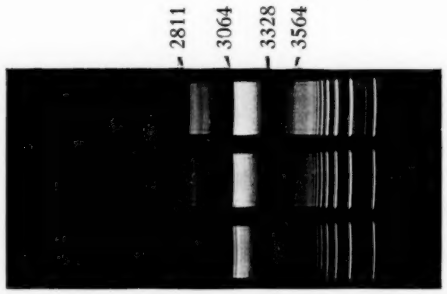

FIG. 1. Electrodeless discharge. 0.1 mm pressure.

structure and since they appear only in the condensed discharge are to be attributed to an ionized radical. As water of high purity was used to supply the vapor it seems probable that the carrier is OH^+.

These bands always appear with a condensed discharge at pressures low enough for the discharge to have a red color. At higher pressures the discharge is bluish white and these bands are not obtained.

The spectrum of the electrodeless discharge at low pressures, taken on a small Hilger spectrograph is shown in Fig. 1. In Fig. 2 the same spectrum is shown with large dispersion. The

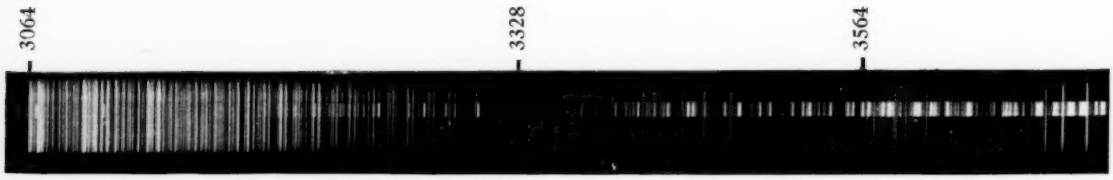

FIG. 2. Electrodeless discharge. 0.1 mm pressure.

new bands at 3564 and 3328A are easily seen as well as the well-known hydroxyl bands. Figs. 3, 4 and 5 are photographs of the discharge in water vapor in a Wood tube, with aluminum electrodes. The new bands appear only at low pressures and when a condensed discharge is used.

Stewart and Lavin[9] have reported that they obtained the OH bands in emission apparently as an afterglow from the dark part of the tube 30 cm from the discharge. This point was investigated and it was found that under ordinary conditions a faint discharge travelled throughout the apparatus which gave the hydroxyl bands with considerable intensity. When elaborate precautions were taken in the way of shielding to

[8] Professor F. W. Loomis of the Department of Physics has undertaken the analysis of these bands. A preliminary note, reporting their discovery was published; J. Am. Chem. Soc. **55**, 1742 (1933).

[9] Stewart and Lavin, Proc. Nat. Acad. Sci. **15**, 829 (1929).

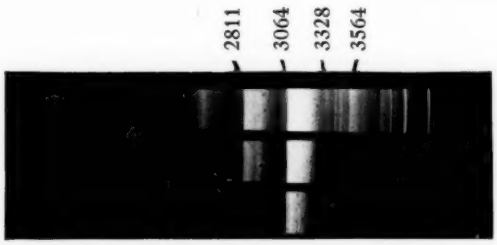

FIG. 3. High frequency electrode discharge. 0.1 mm pressure.

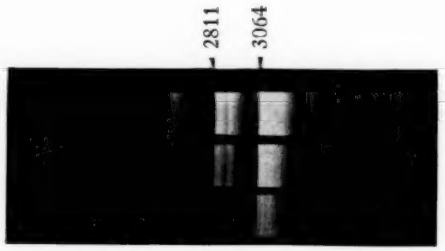

FIG. 4. High frequency electrode discharge. Several mm pressure.

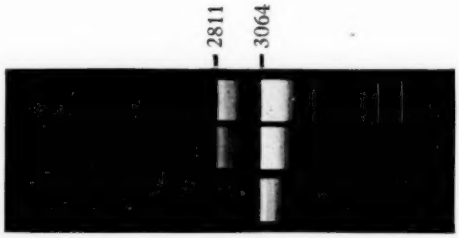

FIG. 5. 60 cycle electrode discharge. 0.1 mm pressure.

prevent the discharge, no trace of the hydroxyl bands appeared after fifteen minutes exposure on the small spectrograph.

DISCUSSION

The reaction mechanism proposed by Bonhoeffer and Pearson to account for the disappearance of hydroxyl cannot be correct since large amounts of hydrogen peroxide were obtained in these experiments. The difference in the experimental results is undoubtedly due to the fact that the electrodeless discharge was used and the powerful catalytic action of traces of sputtered metal avoided.

The failure of Bonhoeffer and Pearson to obtain the absorption spectrum should not be difficult to explain. On the other hand we are inclined to agree with their conclusion that hydroxyl disappears by some one fast reaction mechanism so that its concentration is always low and the molecule is not available for other reactions. A low concentration of hydroxyl is not inconsistent with a high intensity of emission of the hydroxyl bands since it is the *water molecule which is excited to give the hydroxyl bands.* We suspect that the reaction by which hydroxyl disappears is the rapid homogeneous bimolecular condensation to hydrogen peroxide,

$$OH+OH=H_2O_2. \qquad (3)$$

The energy liberated here is about 41 large calories. This amount of energy would correspond to the excitation of the hydroxyl to the fifth vibrational state and the disposal of this energy does not seem to be a serious obstacle to the reaction.

Heterogeneous reactions do not occur rapidly unless adsorption takes place upon the walls of the vessel and experience has shown that minimum of catalytic wall activity is obtained when considerable amounts of water vapor are present. Since large concentrations of hydrogen atoms were shown to reach the liquid air trap the wall activity was certainly slight. The only alternative to bimolecular reactions are those taking place in triple collisions and these must of necessity be slow reactions.

The above reaction mechanism should be very rapid, causing the disappearance of hydroxyl immediately after leaving the discharge. About 50 percent of the water is converted to hydrogen peroxide. It is not likely that much more than 50 percent of the water molecules are dissociated in the first place and there are reactions which could account for the reconversion of considerable amounts of hydrogen peroxide to water. With a more intense discharge a considerable amount of atomic oxygen is produced probably by the dissociation of free hydroxyl. But at moderate intensities the amount of oxygen produced is negligible. The results of Bonhoeffer and Pearson who obtained only traces of hydrogen peroxide are accounted for by the presence of particles of metal sputtered from the electrodes.

Our experiments show that hydrogen peroxide vapor is decomposed quantitatively by small amounts of exposed metal surface into water and oxygen.

The evidence for the above reaction is negative and falls into two classes. First, one must assume that if hydrogen peroxide were not formed by simple, rapid, mechanism that competing reactions would take place. The most important of these is the reaction with atomic hydrogen.

$$H+OH=H_2O-115 \text{ cal.} \quad (4)$$

The energy to be disposed of here is probably too large to permit a bimolecular mechanism.

Finally it is necessary to consider other possible reactions by which hydrogen peroxide may be formed. It is necessary to consider only those mechanisms which are sufficiently simple to be inherently probable. There are two mechanisms which form hydrogen peroxide directly.

$$O+H_2O=H_2O_2-33 \text{ cal.} \quad (5)$$

$$OH+H_2O=H_2O_2+H+72 \text{ cal.} \quad (6)$$

The first reaction is inherently improbable as it involves a change from a triplet to a singlet state and it was shown in this work not to take place either in the main part of the apparatus or in the liquid air trap. The second reaction cannot take place because of the large amount of heat absorbed.

It was shown in this work and has been shown previously by Bates[10] and others that atomic hydrogen reacts with molecular oxygen to give hydrogen peroxide by some mechanism which is presumably complex and hence not very rapid. There are two mechanisms by which molecular oxygen might be formed.

$$OH+OH=H_2+O_2 \quad (7)$$

$$OH+OH=H_2O+O. \qquad O+O=O_2 \quad (8)$$

The first reaction has a high heat of activation since the reverse reaction has a high heat of activation and the heat of reaction is small. The second mechanism is controverted by the experimental evidence as to the concentration of atomic oxygen. Furthermore the formation of molecular oxygen by these two steps must be exceedingly slow. Also to produce a 50 percent conversion to hydrogen peroxide 100 percent dissociation of water molecules would be necessary. There is reason to believe as has been mentioned that the conversion to hydrogen peroxide is much greater than observed since the reaction

$$H+H_2O_2=OH+H_2O$$

must take place to some extent particularly on the walls of the trap.

The experiment with the discharge only three cm from the trap with a flow rate of 9 meters per second shows that the reaction probability per collision from hydroxyl by (3) must be of the order 10^{-3}. It is unlikely that any competing reaction can be found which is as fast.

There is of course no direct proof that the condensation of hydroxyl does not take place on the walls of the trap and undoubtedly this reaction does take place to some extent. The fact, however, that no variation in yield of peroxide with distance of trap or rate of flow was observed, is most easily explained by assuming the disappearance of hydroxyl by a gas phase reaction which is faster than any competing reaction.

If we assume that the new bands observed are due to OH^+ then the fact that they appear only at low pressures tends to confirm the hypothesis of the reaction mechanism. While the absolute amount of hydroxyl present will decrease with decreasing pressure the relative amount will increase and this will result in the formation of an increased amount of OH^+. This conclusion can only be true if the disappearance reaction for hydroxyl is of second or higher order.

The authors wish to express their gratitude to Professor F. W. Loomis for the loan of spectrographic equipment and for advice in the interpretation of spectra.

[10] Bates and Salley, J. Am. Chem. Soc. **55**, 110 (1933).

Complex Formation due to Polarization. I. The System Krypton and Hydrogen Chloride

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Rare gases form compounds of a loose complex nature such as hydrates, solvates or mercury complexes. Such molecular aggregates contain a molecule of permanent dipole moment or an excited atom or molecule of dipole character as the other reaction partner besides the rare gas. The forces holding the complex molecule are the attraction between the permanent dipole and the dipole induced in the rare gas molecule due to its polarizability. Five lines of evidence are cited which indicate the formation of such complex molecules: (1) Band spectra of complex HgA and HgKr are known. (2) Rare gas hydrates have been described. (3) Isoelectronic systems similar to the rare gases have proton affinity. (4) Rare gas hydride ions have been found in the mass-spectrograph. (5) The P-V-T relation of gaseous mixtures show that interaction between the unlike molecules exists. The second Virial coefficient is determined experimentally for Kr−HCl mixtures as a function of composition and it is shown that interaction exists between the rare gas atom Kr and the permanent dipole HCl.

INTRODUCTION

THE rare gases are usually considered to be chemically nonreactive although periodically the preparation of some chemical compounds involving rare gases is announced.[2] In this paper we wish to discuss this question and make clear the distinction between "primary valency compounds" and "complex molecules" involving the rare gases. Whenever the possibility exists for the formation of an electron pair,[3] then the usual valency forces are acting. However, the further possibility exists that atoms which cannot react in the normal state with other atoms or molecules may still form complex structures on account of the van der Waals force field[4] which surrounds them. It will be shown that hydrate formation and the behavior of rare gas molecules toward dipole structures in general give evidence of such loosely bound molecular complexes held together by polarization forces.

One of the latest attempts to produce chemical compounds involving a rare gas has been described by Antropoff[5] who has studied the reaction between chlorine and krypton in electrical discharge. He believes that a compound "krypton chloride" is possible. That such a compound cannot be held together in the ordinary way by primary valency forces, may be shown quite definitely by the use of thermodynamic arguments involving a Born-Haber cycle. Grimm and Herzfeld[6] show that hypothetical KrCl is endothermic to the extent of 95,000 calories. If it be supposed that the compound be salt-like with chlorine as the positive ion in the crystal-lattice, then it can be shown that the hypothetical "chlorine kryptide" would be endothermic to the extent of 165,000 calories, if the electron affinity of Kr is zero and the grating energy is that of RbCl. Either of the two structures considered seems then energetically impossible mainly because of the high ionization potentials. If the two elements krypton and chlorine really combine, then the resulting compound must have a different structure from the salt-like configurations assumed so far. The bond of the hypothetical molecule KrCl may be made between an excited state of krypton and

[1] This article is based upon a thesis presented to the faculty of the Graduate School of the University of Minnesota by Charles P. Roe in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Gmelin-Kraut, Handbuch Inorg. Chem. 8th Edition. Verlag Chemie, Leipzig-Berlin (1926). Mellor, Inorg. Chem. Vol. VII, Longmans, Green & Co., London (1927).

[3] G. N. Lewis, *Valence and the Structure of Atoms and Molecules*. Chemical Catalog Co., N. Y. (1923). Heitler and London, Zeits. f. Physik **44**, 455 (1927).

[4] F. London, Zeits. f. physik Chemie **11B**, 222 (1931).

[5] A. von Antropoff, Naturwiss. **20**, 688 (1932).

[6] Grimm and Herzfeld, Zeits. f. Physik **19**, 141 (1923).

the normal state of chlorine, and the resulting energy rich molecule may at least have transient existence. Compounds of the rare gases of the ordinary valence type are then not to be expected and we shall next consider the evidence for more loosely bound structures or complex molecules of a van der Waals type.

Evidence from Bandspectra

Complex molecules which have their origin in the combination of one excited and one unexcited atom are well known in band spectroscopy.

Oldenberg[7] has studied band spectra excited by fluorescence with λ2537A in mixtures of rare gases and mercury vapor, and he explains these spectra by means of the assumption that molecule formation is possible not only between normal rare gas atoms and excited mercury atoms

$$A(^1S)+Hg(^3P)\rightarrow A\cdot Hg^*,$$

but that normal atoms of the two species considered can also combine into loosely bound structures of the type HgKr and HgA:

$$A(^1S)+Hg(^1S)\rightarrow HgA;\ \Delta H=0.025\text{ e.v.}$$

$$Kr(^1S)+Hg(^1S)\rightarrow HgKr;\ \Delta H=0.035\text{ e.v.}$$

The small value of the heat of dissociation is readily understood, for the forces acting between these atoms are due to their mutual polarization. Oldenberg favors the view that the normal state of these molecules has a definite system of vibrational levels and a definite heat of dissociation. Another interpretation due to Condon[8] is to suppose that the normal state of the complex molecule A·Hg is essentially repulsive and that maxima of intensity in the true continuum are really not bands in the ordinary sense but are due to the oscillatory behavior of the wave functions describing the system and its transitions. The possibility of such interaction exists because the excited mercury atom possesses a high dipole moment, and it can therefore polarize the rare gas atom. The same type of interaction might then be expected between normal rare gas atoms and other normal atoms or molecules possessing permanent dipole moments such as hydrogen chloride and water resulting in the formation of a structure of greater complexity.

Rare Gas Hydrates

The formation of hydrates of gases was studied very early[9] and the heavier rare gases form such hydrates. It is interesting to note that the stability of the rare gas hydrates increases with increasing atomic weight and polarizability of the rare gas.

Isoelectronic Systems

However, an entirely different point of view gives rise to the same ideas. This point of view is based on octet theory of atomic structure and has been stated by Grimm.[10] An atom and a molecule are said to be isoelectronic systems if they have the same outer electronic configuration. They are also called pseudo-atoms. For example hydroxyl ion (OH^-) is a pseudo atom of fluorine. Table I gives such related structures. The formation of NH_4^+ and H_3O^+ follows very simply on the basis of these considerations. A study of the table immediately suggests that perhaps neon and methane may possess a slight proton affinity like water and ammonia. This entirely different view then leads also to an understanding of the existence of hydrates of the rare gases and it suggests possible complex structures between rare gas molecules and hydrogen chloride. This point of view would, however, lead one to consider these structures as "primary valency" compounds.

Table I. *Isoelectronic systems.*

				Ne	Na^+
			F	HF	*NeH*$^+$
		O	OH	H_2O	$H_2F(?)$
	N	NH	NH_2	NH_3	H_3O^+
C	CH	CH_2	CH_3	CH_4	NH_4^+
					CH$_5^+$

Application of Quantum Mechanics

Recently quantum mechanics has been applied to this problem with considerable success. The

[7] O. Oldenberg, Zeits. f. Physik **55**, 1 (1929).

[8] E. U. Condon, Phys. Rev. **32**, 858 (1928).

[9] M. de Frocrand, Comptes Rendus **135**, 959 (1902); M. P. Villard, Thesis, Paris, 1896.

[10] H. Grimm, Zeits. f. Electrochemie **31**, 474 (1925).

simplest case of proton affinity has been studied by Unsöld[11] who has given a theoretical solution of the problem: $H+H^+\rightarrow H_2^+$. The problem of weak or van der Waals molecules has been considered by Eisenschütz and London[12] who give a perturbation method for the calculation of the mutual energy of two molecules at large separation. In this calculation the following forces are considered: (1) the mutual interaction from the electronic motions of the molecule; (2) the polarization of the electron shell of one atom by a permanent field of the other when the latter possesses electric asymmetry; and (3) the ordinary electrostatic forces between two asymmetric molecules. London[4] was thus able to calculate the order of magnitude of van der Waals a and to find the heats of such reactions as

$$Hg+Hg\rightarrow Hg_2,\ \Delta H=2000 \text{ cal.}$$

$$Hg+A\rightarrow HgA,\ \Delta H=1450 \text{ cal.}$$

$$Hg+Kr\rightarrow HgKr,\ \Delta H=1720 \text{ cal.}$$

In all cases the results are in good agreement with the band spectra evidence mentioned above.[7] Margenau[13] has extended the problem by calculating interactions due to quadrupoles.

Mass-Spectroscopy

Consideration of Table I shows that the rare gas atoms may have a tendency to combine with charged ions to form more complex gaseous ions of the type HeH^+, NeH^+, etc. It is interesting to note that workers in the field of mass-spectroscopy have found evidence of such structures. The following ions have been observed:[14–17] $(HeH^1)^+(5)$, $(HeH^2)^+(6)$, $(HeH^1H^1)^+(6)$, $(NeH)^+(23)$ and $(AH)^+(41)$. The experimental evidence favors the view that the proton is outside the nucleus because in the case of helium for example the mass found is 5.01 and not 5.00 which latter value would be expected if the ion considered were an isotope of helium.

Intermolecular Forces

It was expected that some evidence of molecule formation could be obtained at high pressures by studying the pressure-volume-temperature relations of gaseous mixtures of krypton and hydrogen chloride. By such experimental studies we hope to contribute evidence for the existence of loose complex molecules involving the rare gases. A good summary of the theory of imperfect gases has been given by Fowler.[18] According to this treatment the theory of molecular interaction in a binary gas mixture leads to the following equation

$$PV=RT+BP \text{ (for one mole of gas)} \quad (1)$$

where

$$B=b_{11}(1-x)^2+2b_{12}(1-x)x+b_{22}x^2 \quad (2)$$

and

$$b_{\alpha\beta}=\int_{V_{\alpha\beta}}(e^{-E_{\alpha\beta}/RT}-1)dW_\beta \quad (3)$$

and P = pressure, T = abs. temperature, R = gas constant, B = second virial coefficient, x = mole fraction of gas No. 1.

$E_{\alpha\beta}$ = interaction energy between molecule α and β, where α and β may refer to the same or to different species. From these equations it is seen that $b_{\alpha\beta}$ will be zero if $E_{\alpha\beta}$ is zero. In other words *the existence of interaction between molecules of type α and type β can be determined by studying the second virial coefficient B and noting whether or not the interaction term b_{12} is necessary for the description of B as a function of composition.* This study is made by investigating the pressure-volume-temperature relations of a gaseous mixture such as krypton and hydrogen chloride. Krypton was chosen because it has a high polarizability and no chemical reactivity in the ordinary sense; hydrogen chloride was chosen because it has a large permanent dipole moment.

Apparatus

An apparatus has been designed for studying the pressure-volume-temperature relations of

[11] A. Unsöld, Zeits. f. Physik **43**, 563 (1927).

[12] Eisenschütz and London, Zeits. f. Physik **60**, 491 (1930).

[13] H. Margenau, Phys. Rev. **38**, 747 (1931).

[14] T. R. Hogness and E. C. Lunn, Phys. Rev. **26**, 44 (1925).

[15] H. Lukanow and W. Schütze, Zeits. f. Physik **82**, 610 (1933).

[16] K. T. Bainbridge, Phys. Rev. **43**, 103; **44**, 57 (1933).

[17] H. Kallmann and W. Lasareff, Naturwiss. **20**, 206 (1932).

[18] R. H. Fowler, *Statistical Mechanics*, Ch. VIII, page 171, Eq. (487). Cambridge University Press, 1929.

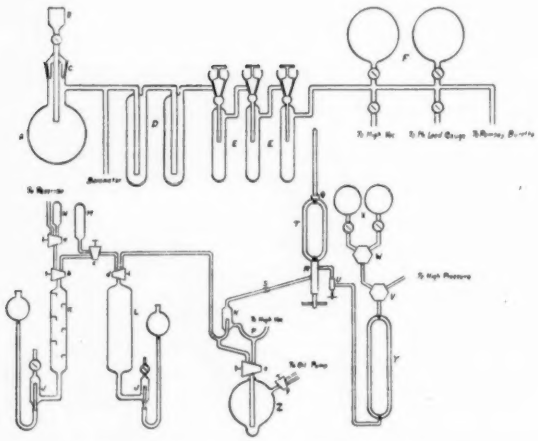

FIG. 1. General plan of experimental system.

systems between −40°C and +250°C and at pressures from 1 to 200 atmospheres. A general outline is given in Fig. 1. An improvement over the usual Cailletet apparatus[19] was made by connecting permanently the high pressure parts of the system to the supply and vacuum sections so that it was unnecessary to dismantle the capillary for each refilling. The hydrogen chloride is generated in flask *A* from H_2SO_4 and NaCl, dried with P_2O_5, purified by sublimation and stored in flask *F*. The krypton was obtained from a commercial source and was not further purified. The pure or mixed gases were measured in the Ramsay burette *K* and run into the Toepler pump *L*. The needle valve *U* was closed and the large valve *R* was opened and the entire system to stopcocks *d* and *e* evacuated to 10^{-4} mm Hg. Now the gas in *L* was led into the cylinder *T* (1000 cc) and capillary *Q*. After *R* was closed *U* was opened and the gas compressed with mercury as a confining liquid. The upper part of *Y*, which was connected directly to the gauge tester by means of the joint at *V*, was filled with glycerine; the lower end of *Y* was filled with mercury. This arrangement was necessary in order to prevent mercury from making contact with the gauge tester. The gauges which were calibrated with the piston tester are shown at *X*.

In making the *P*−*V*−*T* measurements the pressure was noted when the mercury meniscus just reached one of the eight finely etched calibrating marks on the capillary which was 40 cm long and 0.2 cm internal diameter. The temperature was easily controlled by the vapors of ether, acetone, ethyl alcohol, and propyl alcohol at their boiling points. The capillary was surrounded by a long unsilvered Dewar flask (20×3″), and was calibrated by weighing the amounts of mercury between the marks. This was done by sealing the end of the capillary and filling to the desired mark with mercury from a still finer capillary. A correction was made for the inverted meniscus.

[19] K. Jellinek, Lehrbuch d. Phys. Chemie, Vol. I, pp. 310–936. F. Enke, Stuttgart (1928).

DATA AND RESULTS

We shall only give a summary of a large amount of data on krypton and hydrogen chloride and their mixtures. The *PV*−*P* relations are shown for two temperatures in Fig. 2 and the needed data are collected in Table II.

TABLE II. *PV*−*P measurements for krypton-hydrogen chloride mixtures. X = mole fraction HCl.*

T \ X	P	0	0.263	0.492	0.729	1.000
95.5°C	0	1.350	1.350	1.350	1.350	1.350
	20	1.328	1.328	1.325	1.301	1.286
	40	1.305	1.310	1.295	1.249	1.207
	60	1.283	1.277	1.248	1.189	1.112
	80	1.261	1.243	1.203	1.123	1.006
	100	1.239	1.217	1.167	1.066	0.902
55.5°C	0	1.203	1.203	1.203	1.203	1.203
	20	1.170	1.184	1.164	1.144	1.112
	40	1.137	1.144	1.115	1.073	0.997
	60	1.104	1.097	1.052	0.980	0.845
	80	1.072	1.054	0.995	0.881	0.626
	100	1.038	1.018	0.935	0.780	—

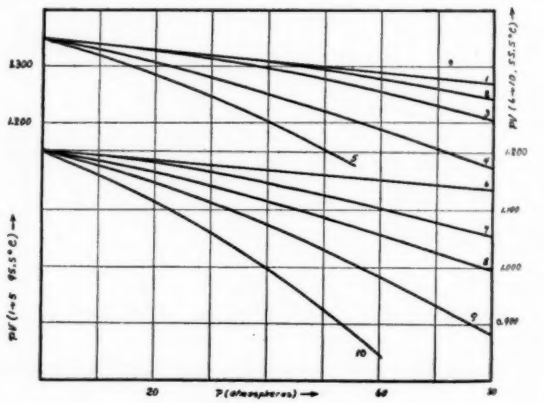

FIG. 2. *PV*−*P* isothermals for HCl-krypton mixtures. (*PV*=1 when *P*=0 and *T*=0°C.) Data for curves 1–10 from Table III.

TABLE III. *Experimental values of B. Kr−HCl.*

$-B=0.00114(1-X)^2+0.00102(1-X)X+0.00309X^2$						
10 atm. 95.5°C	X	0	0.263	0.492	0.729	1.000
	$-B$	0.00111	0.00112	0.00123	0.00192	0.00310

$-B=0.00168(1-X)^2+0.00194(1-X)X+0.00445X^2$						
10 atm. 55.5°C	X	0	0.263	0.492	0.729	1.000
	$-B$	0.00165	0.00169	0.00196	0.00283	0.00447

The data were calculated from the original observations taking $PV=1$ at $P=0$ and $T=0$°C. The $PV-P$ curves are given at two temperatures: 55.5° and 95.5°C. Each family of these curves represents mixtures of different compositions for one temperature. It is seen that the second virial coefficient is a function of the pressure at the temperature considered, with exception of pure krypton where curves 1 and 6, Fig. 2, are straight lines over the pressure range studied.

DISCUSSION OF RESULTS

Lennard-Jones[20] has shown that for mixtures of molecules with *spherically symmetrical* fields of force, the coefficients b_{11}, b_{12} and b_{22} are given by

$$b_{\alpha\beta}=2\pi\int_0^\infty r^2(e^{-E_{\alpha\beta}/RT}-1)dr$$

where $E_{\alpha\beta}$ is the interaction energy between molecules α and β and from experimental data he was able to find the constants λ, μ, m and n in the force equation

$$\partial E_{\alpha\beta}/\partial r=f(r)=\lambda/r^n-\mu/r^m.$$

In the system HCl−Kr however *the interaction energy is not dependent on r alone but also depends on the angles θ and φ because hydrogen chloride is an asymmetric molecule of dipole character.* The simplified treatment given above is therefore not possible in the case studied. However, it still is possible to show interaction between hydrogen chloride and krypton despite the fact that the force constants cannot be evaluated. Although the second virial coefficient is a function of the pressure at any temperature, it is found that at a given pressure (10 atmospheres for example) B is still a quadratic function of the composition.

[20] Lennard-Jones, Proc. Roy. Soc. **A106**, 463 (1924).

Since it is of primary interest to show that b_{12} does not vanish for the case of the system in question, the analytical evaluation of the above integral becomes unnecessary. For B, the second virial coefficient for the mixture, can be experimentally determined as a function of composition. When the data obtained from the pressure volume measurements were used to determine the best parabola that could be fitted to the experimental points, it was definitely found that b_{12} was different from zero in the equation of this parabola. It should be noted, that even if $b_{12}=0$, the resulting form of B is still a parabola, that is,

$$B=b_{11}(1-x)^2+b_{22}x^2,$$

and this parabola can be obtained directly from the pressure volume data for the two pure gases. It is immediately found however, that this is in marked disagreement with the experimental facts. The situation is clearly pictured in Fig. 3, where the experimental points are shown by the circles, the best parabola that can be passed through them by the solid line, and the simplified parabola, that is with b_{12} set equal to zero, by the broken line. This last procedure amounts to the omission of interaction between the unlike mole-

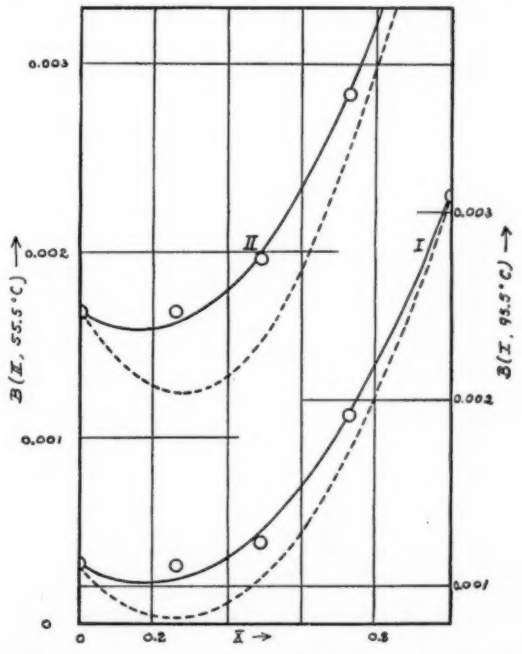

FIG. 3. $B-X$ curves for HCl-krypton mixtures. Unbroken curve, $B=b_{11}(1-x)^2+b_{12}(1-x)x+b_{22}x^2$. Broken curve, $B=b_{11}(1-x)^2+b_{22}x^2$.

cules Kr and HCl, while the interaction between like molecules is still considered. It is seen that the resulting dotted curves *do not fit the experimental curves nearly as well as do the parabolas including interaction between unlike molecules.*

The $P-V-T$ relations studied here give then evidence of interaction between a rare gas atom and a permanent dipole molecule. The interaction term b_{12} is seen to be of the same order of magnitude and of the same sign as the terms b_{11} and b_{22} thus indicating attractive forces (Table III). This result is in keeping with the other lines of evidence obtained from band spectroscopy, hydrate formation, the general behavior of isoelectronic systems (pseudo-atoms) and their proton affinity. This behavior can best be understood on the basis of modern wave mechanics as studied by London.[4]

Complex Formation due to Polarization. II. The System Propane and Hydrogen Chloride

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Molecules of saturated hydrocarbons are rare gas-like in structure and they may be supposed to behave in many respects like rare gases. They may then be expected to show complex formation with other molecules or atoms of dipole character, depending on their own polarizability (preceding article). An experimental study of the *P-V-T* relations of the gaseous mixtures of propane and hydrogen chloride shows that interaction does indeed take place between these two types of molecules. The expression for the second virial coefficient as a function of composition of the gaseous mixtures, is shown to require an interaction term between unlike molecules in order to agree with experiment. This question of complex formation of saturated hydrocarbons is further discussed on the basis of Brönsted's theory of acids and bases.

INTRODUCTION

IN a former paper[2] the question was discussed as to whether or not rare gas atoms had any chemical properties in the sense that they could react with other atoms or molecules to form chemical compounds. It was shown that compounds of the usual valency type were energetically unstable if they involved a rare gas atom as one of the reaction partners. However, evidence was cited to show that the rare gases could form loosely-bound structures with other molecules and that such complexes could be more easily formed if the rare gas in question had a large polarizability and if the other reaction partner had a high dipole moment. It is, of course, well known that methane for example is very much like a rare gas.[3] It may then be expected that rare gas-like molecules such as methane should show a similar behavior to the rare gases in the sense that methane should show no further chemical reactivity by *addition*. That is, primary valency compounds of methane which involve an electron pair either by sharing or transfer are probably energetically impossible, and they are not known. However, secondary complexes of the hydrate type may be expected. More generally solvates may be formed or at least a further interaction between a hydrocarbon of large polarizability and a permanent dipole molecule or an excited atom may be possible.

HYDRATES OF HYDROCARBON MOLECULES

Hydrocarbon molecules may then form complex secondary structures with molecules such as water, especially if, they themselves have large polarizabilities. Hydrates of the hydrocarbons have been described by Frocrand[4] (Table I) and

TABLE I.

	CH_4	C_2H_6	C_3H_8	C_2H_4	C_2H_2
Polarizability $\alpha\times10^{24}$	2.6	4.5	6.3	4.0	3.5
Hydrates	$6H_2O$	$7H_2O$	—	$7H_2O$	$6H_2O$

these complex secondary structures seem to be held together by forces due to the induced polarization of the hydrocarbon and the consequent interaction of the field of the induced dipole with that of the permanent dipole of the water molecule.

ISOELECTRONIC SYSTEMS

Just as the consideration of isoelectronic systems in the case of rare gases led to the view

[1] This article is based upon a thesis presented to the faculty of the Graduate School of the University of Minnesota by Donald L. Fuller in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] See preceding article, J. Chem. Phys. **1**, 703 (1933).

[3] Geo. Glockler, J.A.C.S. **48**, 2021 (1926).

[4] M. deFrocrand, Comptes Rendus **135**, 959 (1902).

that they may have a small residual affinity for protons, so again it may be supposed that the rare gas-like hydrocarbons should have a similar property. For our purposes the important question suggested by the theory of pseudo-atoms is: Does the methonium ion exist? That is, is it conceivable that a proton may enter the complete octet of methane or a similar hydrocarbon in accordance with the equation:

$$CH_4+H^+\rightarrow CH_5^+.$$

At once it is realized that high polarizability of the hydrocarbon molecule would be advantageous, for then the forces of interaction would be largest. The idea that a complete structure like a saturated hydrocarbon can react further with other molecules by addition arises then in two ways: (1) because of its polarizability other molecules or ions can further interact with it; and (2) it may have a proton affinity like an isoelectronic system of similar structure. These two points of view remind one strongly of the situation encountered in discussing so-called primary valency compounds on the basis of ordinary valency principles, and on the basis of Werner's theory of coordination compounds.

Brönsted Theory of Acids and Bases

The question raised as to a possible proton affinity of saturated hydrocarbon molecules can be put into another language. It can be asked: Has the methane molecule any acidic or basic properties? On the principle of Brönsted,[5] that any substance able to give up a proton is of acid character and any substance able to take on a proton is of basic character, the above question is quite proper. On these modern views such molecules as ammonia and water are basic in nature when it is considered that they will add protons to form ammonium and hydronium ions. But they also ionize to a slight extent into hydrogen ions and they therefore exhibit also acid properties. Ultimately it is found to be the surrounding medium which determines the predominant acidic or basic characteristics of the substance in question. In this way it may be expected to find that methane acts like a base if it is brought into contact with a substance which gives protons readily, that is, an acid in the Brönsted sense. Of course the basic character of methane may be very weak and it may be difficult to discover evidence of it. However, the formation of hydrates noted above seems to indicate that even such a symmetrical molecule as methane shows the incipient stages of basic action. Substitution of other radicals for the hydrogen atoms of methane will no doubt have great influence upon the basic or acidic character of the resulting molecule. Such methano acids and bases have been considered by E. C. Franklin.[6] The basic and acidic character of the highly symmetrical methane molecule would be expected to be very slight but, to deny the existence of these properties would be to remove a very reasonable method of accounting for these hydrates. While the possible basic character of saturated hydrocarbons is the main topic for consideration in this paper it is of interest to recall that the acid character of substituted methanes is very marked as pointed out by Franklin. For example the substitution of a "CH" radical for three of the hydrogen atoms of the molecule of methane will make the hydrogen atom in the resulting acetylene so "acidic" that it is easily replaceable by metals such as silver and copper, and the well-known acetylides result. Cyclopentadiene, indene and fluorene are hydrocarbons which behave in the same manner. They have hydrogen atoms in their structure which are replaceable by metals and Franklin considers these structures as substituted methano acids. It seems then possible to consider that methane is amphoteric in character like ammonia and water.

$$NH_3+H^+\rightarrow NH_4^+$$
$$NH_3\rightarrow NH_2^-+H^+$$

$$H_2O+H^+\rightarrow H_3O^+$$
$$H_2O\rightarrow H^++OH^-$$

$$CH_4+H^+\rightarrow CH_5^+$$
$$CH_4\rightarrow H^++CH_3^-$$

While such reactions of methane probably happen only to a very slight extent, the possibility of such behavior must be admitted.

[5] J. N. Brönsted, Chem. Rev. **5**, 231 (1928).

[6] E. C. Franklin, J.A.C.S. **46**, 2137 (1924).

Band Spectroscopy and Quantum Mechanics

While evidence of a very interesting nature was at hand for "rare gas mercury" molecules obtained by Oldenberg[2] who showed the existence of band spectra carried by complex molecules, and while further progress is being made in their interpretation[7] no such experimental evidence has as yet been procured for rare gas-like molecules such as the saturated hydrocarbons.[8] The quantum mechanical arguments of London[9] on the other hand are entirely general, and they are therefore applicable to the case at hand, and on this basis one might again predict with confidence that saturated hydrocarbons can interact with permanently polar molecules or with excited atoms which have dipole moments due to their excitation.

Mass-Spectroscopy

Lukanow and Schütze[10] mention the possibility that ions of mass 17 could be hydroxyl ions (OH^+) or methonium ions (CH_5^+) and they find ions of mass 18 (H_2O^+ or CH_6^+) and mass 31 ($C_2H_7^+$). In themselves these experiments furnish no proof that these ions possess the proposed structures, but taking these suggestions together with similar ideas regarding complexes between rare gases and protons they stand in a better light than that of mere speculation. Such charged ions should as a matter of fact be really more stable than the neutral complexes studied in this research, because the forces acting between an ion and a polarizable molecule will be stronger at a given distance of separation than in the neutral case. It is also interesting to remember in this connection that the existence of the ion H_3^+ is fully established by the methods of mass-spectroscopy[11] while the evidence for the existence of H_3 molecules is mostly negative. The interaction between $H_2+H^+\rightarrow H_3^+$ would be greater than the interaction between $H_2+H\rightarrow H_3$. If a neutral H_3 should be formed in accordance with Heitler-London spin-theory or ordinary valency consideration, then the Pauli principle would have to be considered, and the resulting odd molecule would have one of its electrons in some excited state.

Intermolecular Forces

The various lines of evidence presented so far make it very plausible that a saturated hydrocarbon like "propane" and a dipole like "hydrogen chloride" should form complex structures by interaction. Propane was chosen for experimental investigation because the influence of the two methyl-groups was thought to have a tendency to make the remaining hydrogens on the central carbon atom more "basic" than in the case of methane. It was then expected that interaction could be demonstrated by studying the pressure-volume-temperature relations of mixtures of propane and hydrogen chloride. These experimental data will permit the determination of the "second-virial coefficient" for the various gas mixtures. The variation of this coefficient with composition should then indicate interaction between the unlike molecules of the mixture.[2] The pressure-volume relations should be given by

$$PV=RT+BP \text{ (for one mole of gas)} \qquad (1)$$

where the second virial coefficient is

$$B=b_{11}(1-x)^2+2b_{12}(1-x)x+b_{22}x^2. \qquad (2)$$

The quantities b_{11}, b_{12} and b_{22} are integrals showing the interaction of like and unlike molecules

$$b_{\alpha\beta}=\int_{V_{\alpha\beta}}(e^{-E_{\alpha\beta}/RT}-1)dW_\beta. \qquad (3)$$

The other symbols have the following meanings: P = pressure, T = abs. temperature, R = gas constant, x = mole fraction of gas No. 1.

$E_{\alpha\beta}$ = interaction energy between molecules of type α and β where α and β may refer to the same or different species. The parabola expressed by Eq. (2) is to be determined experimentally for the propane-hydrogen chloride system, and it is to be decided whether or not the term in b_{12} is needed in order to make experiment fit the curve of Eq. (2). It is important to note that the interaction integral b_{12} need not be evaluated in order to find out whether or not interaction between unlike

[7] W. Finkelburg, Zeits. f. Physik **81**, 781 (1933).
[8] Such work is being undertaken in this laboratory.
[9] F. London, Zeits. f. physik. Chemie **11B**, 222 (1931).
[10] H. Lukanow and W. Schütze, Zeits. f. Physik **82**, 610 (1933).
[11] T. R. Hogness and E. C. Lunn, Phys. Rev. **26**, 44 (1925).

molecules exist. It is seen that the integrand is "zero" if the interaction energy $E_{\alpha\beta}$ is zero. This situation applies even if the interaction energy is a function of the angle coordinates as well as of the distance r from the molecule. In the case of interaction involving a dipole like hydrogen chloride the interaction energy is evidently a function of the angles as well as of distance, but still it is possible to use the Eq. (2) to deduce the existence of interaction between propane and hydrogen chloride.

Apparatus, Data and Results

The apparatus used in this study of the pressure-volume-temperature relations of propane-hydrogen chloride mixtures has already been described[2] and we need only show the results of these experiments. The $PV-P$ relations for propane, hydrogen chloride and their mixtures are shown in Fig. 1 and the data are given in Table II. The numbers given were

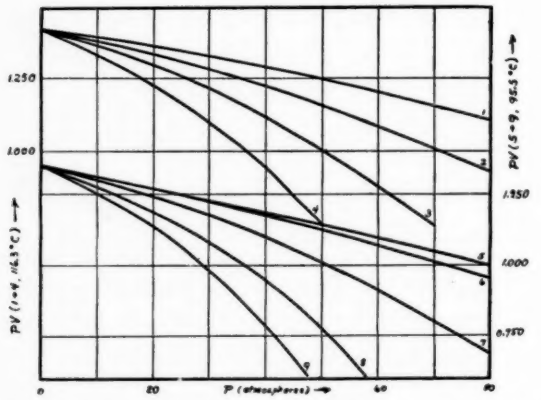

Fig. 1. $PV-P$ isothermals for HCl-propane mixtures. ($PV=1$, when $P=0$ and $T=0$°C). Data of curves 1–9 from Table III.

calculated from the original observations taking $PV=1$ at $P=0$ and $T=0$°C. Two temperatures have been employed: 95.5°C and 116.3°C. From these data the second virial coefficient B has been obtained at 40 atmospheres pressure at the two temperatures for the various mixtures. The best parabolas which will fit the B–X experimental relations have been calculated by the method of least squares. These experimental parabolas are then compared with the expression (2).

Table II. *$PV-P$ measurements for propane hydrogen chloride mixtures. X = mol-fraction of HCl.*

T \ X	P	0	0.236	0.499	0.850	1.00
116.3°C	0	1.423	1.423	1.423	1.423	1.423
	20	1.227	1.290	1.330	1.360	
	40	0.956	1.115	1.220	1.290	
	60		0.880	1.084	1.202	
	80			0.929	1.108	
	100				1.007	
95.5°C	0	1.350	1.350	1.350	1.350	1.350
	20	1.133	1.179	1.242	1.268	1.270
	40	0.786	0.950	1.102	1.174	1.184
	60			0.913	1.070	1.093
	80			0.688	0.955	.994
	100				0.825	.886

Table III. *Experimental values of B. Propane-hydrogen chloride.*

$$-B=0.017(1-X)^2+0.00398(1-X)X+0.00388X^2$$

40 atm. 116.3°C	X	0	0.236	0.499	0.850	1.000
	$-B$	0.01710	0.01075	0.00618	0.00398	0.00370

$$-B=0.022(1-X)^2+0.00484(1-X)X+0.00472X^2$$

40 atm. 95.5°C	X	0	0.236	0.499	0.850	1.000
	$-B$	0.0220	0.0138	0.0095	0.00485	0.00445

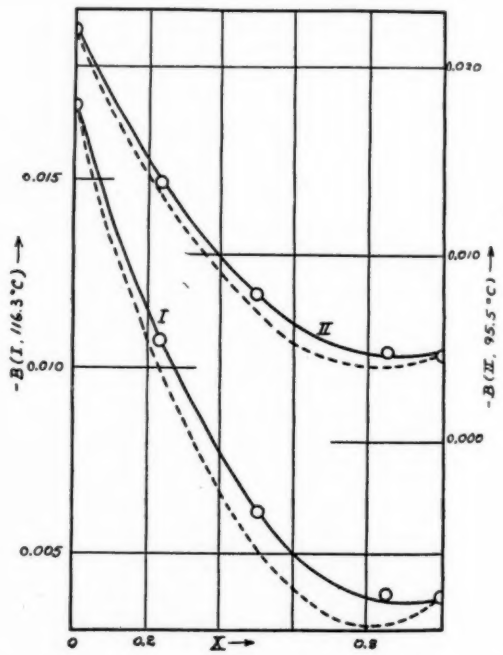

Fig. 2. $B-X$ curves for HCl-propane mixtures. Unbroken curves, $B=b_{11}(1-X)^2+b_{12}X(1-X)+b_{22}X^2$. Broken curves, $B=b_{11}(1-X)^2+b_{22}X^2$.

Discussion of Results

The comparison of the experimental B–X relation with the terms of Eq. (2) is shown in Fig. 2. It is at once seen that the interaction term b_{12} is needed to make experiment fit the theoretical parabola and that it is of the same sign and lies between the values of b_{11} and b_{22}. Therefore these experiments indicate that *propane molecules interact with hydrogen-chloride molecules, and on the basis of the various points discussed* in the introduction it is believed that these results may be taken as further proof for the existence of complex polarization molecules of propane and hydrogen chloride.

Binary Systems in Two Phases. I. HCl−Kr. II. HCl−C_3H_8

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(Received August 7, 1933)

The $P-T-X$ relations of the binary mixtures HCl−Kr and HCl−C_3H_8 have been determined. Retrograde condensation was observed with all mixtures studied. Not more than one liquid phase was found for any of the mixtures.

THE behavior of binary systems in two phases, gaseous and liquid, has been studied by many investigators[1] and very interesting results have been obtained. For example, the phenomenon of retrograde condensation has been discovered for several cases[2] and while theoretical thermodynamic studies which made use of van der Waals equation have not been able to predict this phenomenon, still it has been concluded by several investigators[1] that these phenomena are not excluded by the theory.

In order to extend our knowledge of such binary systems and in order to build up the theory pertaining to them, it seems necessary to study many such systems experimentally over the complete range of temperature, pressure and composition. Very few studies, complete in this sense, have been made[3] and we propose to investigate the mixtures of rare gases and saturated hydrocarbons (lower paraffins) with a dipole gas such as hydrogen chloride. We happened to choose these particular cases because we were interested in the interaction of these respective molecules from the point of view of complex formation. Our whole research program will include the experimental study of any two component system, in the hope that ultimately a comprehensive theoretical treatment will be possible.

APPARATUS

The apparatus built for this study is of the type developed by Cailletet[4] but it has a few novel features which are of general interest. For instance, it is possible in our apparatus to fill the capillary with the various gas mixtures without disconnecting it from the high pressure system. This is a distinct advantage and speeds up operation considerably. Furthermore the whole system could be evacuated to a pressure of 10^{-4} mm Hg by means of a high vacuum system which included a mercury vapor pump, McLeod gauge, etc. The manipulation of the apparatus need not be described in detail since the various operations necessary to obtain the data are obvious, from an examination of Fig. 1, to any one carrying out such experiments. However, a few of the devices

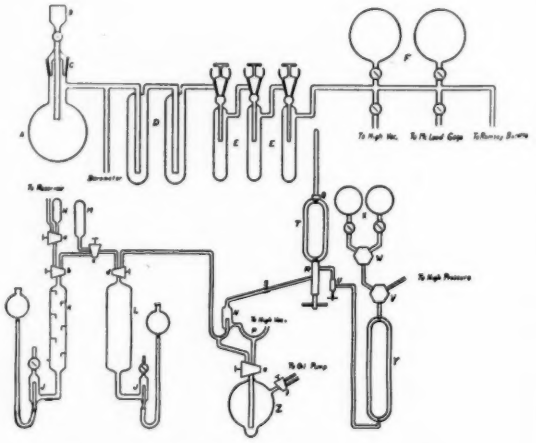

FIG. 1. General plan of experimental system.

[1] van der Waals, *Die Kontinuität des gasförmigen und flüssigen Zustandes*, Vol. II, J. P. Kuenen, *Verdampfung und Verflüssigung von Gemischen*, Verlag, J. A. Barth, Leipzig (1881) and (1906).

[2] Cailletet, Comptes Rendus **95**, 210 (1880) and Kuenen, reference 1.

[3] F. Caubet, Zeits. f. physik. Chemie **40**, 257 (1902); Quint Gzn. Zeits. f. physik. Chemie **39**, 14 (1901).

[4] K. Jellinek, *Lehrbuch der physikalischen Chemie*, Vol. I, pp. 310–936, F. Enke, Stuttgart (1928).

developed in this research seem to deserve a short description.

Packing for high pressure needle valve

Considerable difficulty was experienced with the packing of the high pressure needle valve. We demanded not only that these needle valves be tight against high pressure but also that they be able to withstand evacuation while open. After many trials we finally obtained a Bakelite packing[5] as shown in Fig. 2a which was very

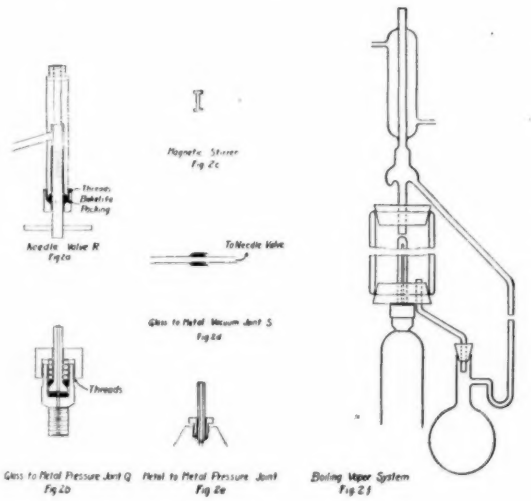

FIG. 2.

satisfactory in every respect. The valve was mounted in a vertical position and it was so arranged that the mercury used as confining liquid would fill any dead spaces. It was possible, by means of a Toepler pump, to transfer a given quantity of gas to and from the "observation-capillary" without loss.

Magnetic stirrer

We noticed that the magnetic stirrers used by former investigators[1] would often show a tendency to stick just at the critical moment when it was desirable to stir the gaseous and liquid phases contained in the capillary. The shape of the magnetic stirrer shown in cross section in Fig. 2c was found to be very satisfactory and we had no difficulty with it. The stirrer was made of iron and it was not covered. By keeping a sample of iron in liquid HCl for a month, we convinced ourselves that liquid hydrogen chloride does not attack iron to any appreciable extent. The amount of gas (presumably hydrogen) formed after this treatment was negligible. A small solenoid used to actuate the stirrer is not shown in the figure.

Other features

Various other joints used are shown in Fig. 2 (b, d, e) which are self-explanatory.[6] For washers we used fiber-board and leather. In order to stop the small magnetic stirrer from falling out of the capillary, we fastened a small platinum wire across the central hole in the lower washer, shown in Fig. 2b.

The measurements were obtained by filling the unsilvered Dewar flask surrounding the capillary with water at a high temperature and letting the system cool. The pressure which the system attained was read at frequent intervals of temperature. The precise technique of making these readings is described in Caubet's article.[3]

RESULTS

The results of this investigation are shown most conveniently as $P-T-X$ diagrams. Such

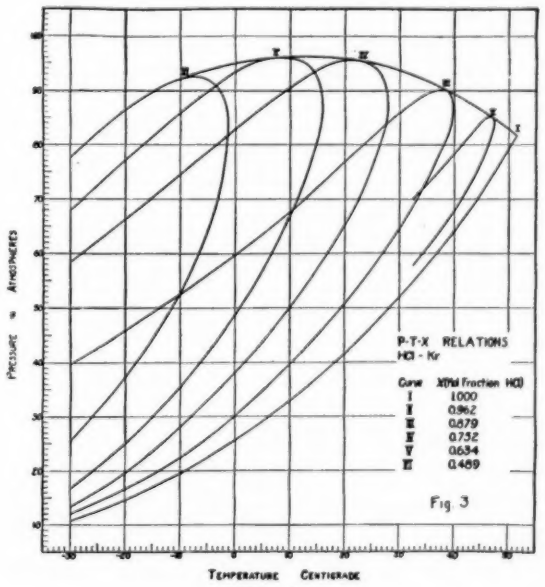

FIG. 3.

[5] We wish to thank Mr. F. W. Fullerton for developing this packing for us.

[6] P. W. Bridgman, *Physics of High Pressure*, The Macmillan Co., New York (1931).

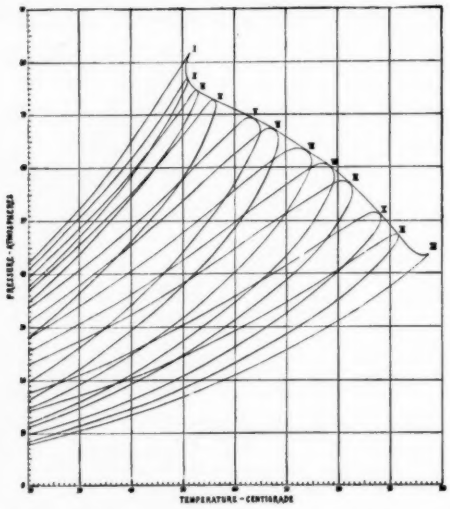

FIG. 4. $P-T-X$ relations, $HCl-C_3H_8$. Curve x (Mol fraction HCl). (Cf. Table II.)

graphs are given in Figs. 3 and 4 for the systems HCl−Kr and $HCl-C_3H_8$.[7] The phenomenon of retrograde condensation was observed in every case and consisted of the following behavior. As the pressure upon the gaseous mixture was increased a liquid phase made its appearance. Further increase in pressure caused the liquid to increase in amount until a maximum was reached, when still greater pressure caused the diminution of the liquid phase until it finally disappeared entirely at a higher pressure. Only one "gas" phase remained. The temperature and pressure ranges in which this phenomenon was observed are mentioned in Tables I and II.

TABLE I. *Retrograde condensation, HCl−Kr.*

	Composition HCl	*Temperature range* (°C)	*Pressure range* (atm.)
I	1.000		
II	0.962	47.0 to 47.5	84.0 to 85.2
III	0.879	38.5 to 39.6	87.0 to 90.0
IV	0.752	23.0 to 28.0	88.0 to 95.4
V	0.634	8.0 to 16.0	87.0 to 96.0
VI	0.489	−10.0 to −1.2	83.5 to 92.7

TABLE II. *Retrograde condensation, $HCl-C_3H_8$.*

	Composition HCl	*Temperature range* (°C)	*Pressure range* (atm.)
I	1.000		
II	0.916	50.8 to 51.0	76.6 to 76.8
III	0.846	52.8 to 53.0	74.0 to 74.5
IV	0.759	56.0 to 56.4	71.6 to 72.6
V	0.617	63.6 to 65.0	67.0 to 69.3
VI	0.522	67.4 to 69.3	65.0 to 67.2
VII	0.449	73.6 to 75.0	61.0 to 63.3
VIII	0.364	78.0 to 79.2	58.0 to 60.4
IX	0.295	82.0 to 82.7	55.0 to 57.2
X	0.170	88.0 to 88.3	50.0 to 51.0
XI	0.090	91.6 to 91.7	46.7 to 47.2
XII	0.000		

Another point to note is the fact that the critical line (marked by Roman numerals in the figures) is quite different for the two systems. Furthermore, only one liquid phase was ever observed for the two systems studied. This would mean that no strong repulsive forces are acting between the different species of molecules studied.[8]

[7] The data for the system HCl−Kr are taken from a thesis presented to the Faculty of the Graduate School of the University of Minnesota by Charles P. Roe in partial fulfillment of the requirements of doctor of philosophy. Similarly the data for the system $HCl-C_3H_8$ are taken from a doctor's thesis by Donald L. Fuller.

[8] J. H. Hildebrand, *Solubility*, Chem.-Catalog Co., New York (1924).

The Atomic Weights of Radioactive Substances[1]

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(Received June 16, 1933)

(1) The isotopic weights of Pb^{206}, Pb^{207}, and Pb^{208}, on the chemical scale O = 16.0000, are obtained by three distinct methods, using in each case the assumption that they differ by an amount very close to unity. The results for Pb^{206} are these: (1) from packing fraction of lead, 205.96_6; (2) from study of the packing fraction curve, 205.99_2; from relative abundance of isotopes in leads of known atomic weight, 206.00_3. Mean, $205.98_7 \pm 0.03$. By taking into account a recent atomic weight determination on lead from Bedford cyrtolite, reasonable rounded values for the three isotopes are 205.98, 206.98 and 207.98 ± 0.03. (2) From these values the isotopic weights of the radioactive substances are obtained by adding the mass (and the mass-equivalent of the energy) lost in disintegration. The calculated values for radium and thorium, 226.02 ± 0.03 and 232.03 ± 0.03, do not agree with the International values 225.97 ± 0.01 and 232.12 ± 0.01. The calculated weights for U^{238} and U^{234} are 238.04 ± 0.03 and 234.04 ± 0.03, respectively, while the heretofore accepted atomic weight of U is 238.14 ± 0.01. In view of Aston's conclusion that U does not contain more than 3 percent of U^{239} or any higher isotope, it appears probable that the accepted value for uranium is somewhat too high. (3) $W - N$ is plotted as a function of N, for the three radioactive series, W being the isotopic weight and N the nearest integer. The graphs obtained are almost linear, and their slopes are nearly identical. In an average way they conform to the equation $W - N = -0.02 + 0.00214\ (N - 206)$.

I. INTRODUCTORY

IF we know the atomic weight of any member of a radioactive series, we can obtain that of any other member by taking account of the masses of the particles emitted, and the mass equivalent of the energy liberated in the disintegrations leading from one of these substances to the other. The errors involved are very small, now that we have precise values for the masses of the electron and the helium atom. Unless otherwise stated, we shall use the chemical scale of atomic weights throughout this paper. Mass-spectrograph results are usually expressed on the scale $O^{16} = 16.0000$. To reduce them to the chemical scale we subtract a correction of 2.2 parts in 10^4, based on the relative abundances of the oxygen isotopes given by Mecke and Childs.[2] Further, we assume that the atomic weight of helium on the chemical scale $= 4.00128 \pm 0.0004$; this is obtained from Aston's value, 4.00216 on the O^{16} scale.[3]

Computations of the atomic weights of radioactive substances were made by Stefan Meyer,[4] but his results differ considerably from those reported here, because he did not have available all the data now at our disposal and because the distinction between the chemical atomic weight scale and the O^{16} scale was not known. Meyer treats uranium as a mixture of U^{238} and 3 percent of a hypothetical isotope U^{239}, thereby computing the weight of U^{238} as 238.011 or 238.010. From this he obtains 226.09 or 226.08 for the atomic weight of radium, a value almost 0.1 unit higher than the accepted one, 225.97. We agree with his conclusion that the chemically-determined atomic weight of radium is wrong, but his value for U^{238} may be questioned, being based on the idea that uranium contains a percentage of U^{239} equal to the actinium-uranium branching ratio, whereas the latter is a ratio of activities, not of masses. Further, Meyer computes the loss of mass between U^{238} and Pb^{206} as 32.07, in close agreement with our value. He then states that if one takes the atomic weight of Pb^{206} + 3 percent Pb^{207} to be 206.05, and adds 32.07, one arrives at 238.12 for the atomic weight of the uranium complex consisting of U^{238} and 3 percent of U^{239}. This lies within the range covered by Hönig-

[1] Preliminary communications may be found in Phys. Rev. **42**, 903 (1932); **43**, 205 (1933).

[2] Mecke and Childs, Zeits. f. Physik **68**, 362 (1931); Aston, Nature **130**, 22 (1932); Naudé, Phys. Rev. **36**, 333 (1930).

[3] See also Bainbridge, Phys. Rev. **43**, 103 (1933).

[4] Meyer, Wien Ber. (IIA) **137**, 647 (1928).

schmid's chemical determinations, and Meyer concludes that no discrepancy exists in regard to the atomic weights of uranium and uranium lead. However, the figure 206.05 is the atomic weight of a lead extracted from Katanga pitchblende (Table I). We know now that it contains 6.7 percent of Pb^{207} instead of 3 percent. Further, as we shall see, there is some evidence against the assumption that uranium contains 3 percent of U^{239}. The entire subject, therefore, must be reconsidered.

II. Weights of the Lead Isotopes

We shall derive the weights of radioactive substances by using the weights of lead isotopes as a base. The latter will be obtained in three ways, namely, from Aston's packing fraction for lead; from the packing-fraction curve; and from the chemically-determined atomic weights of radioactive leads, together with their isotopic compositions.

(1) Aston[5] stated that the packing-fractions of lead isotopes are indistinguishable from the value he gives for mercury, 0.8×10^{-4}. Later he said[6] that the lead packing fractions would be difficult to measure and that they probably lie between zero and $+1\times10^{-4}$. If we place them in the middle of this range we obtain 205.965, 206.965, and 207.965 ± 0.02 for the weights of the principal lead isotopes.

(2) Let W be the weight of an isotope and N the integer nearest to that weight. It is possible to determine the value of $W-N$ for the lead isotopes by studying the dependence of this quantity on atomic weight. The values of $W-N$ are not available for all the individual isotopes of heavy elements. The numbers we shall use are average values for all the isotopes of an element, or values for individual abundant isotopes. Accordingly, we shall simply speak of the $W-N$ value for an element. Aston[7] determined the packing fractions of tungsten, rhenium, osmium and thallium by comparing their lines, or those of their oxides, with the mercury lines; so that any change in the value of $W-N$ for mercury requires corresponding changes in the values for these other elements. Now, from the relative abundances of mercury isotopes and their packing fractions we find the atomic weight $200.60_2\pm0.05$, while the International atomic weight is 200.61 ± 0.004.[8] Thus it seems reasonable to increase Aston's isotopic weights for these heavy elements by half the difference between these numbers, or 0.004. Then for the isotope Hg^{200}, $W-N$ is -0.024. If we plot the resulting $W-N$ values against N, it is found that they do not lie even approximately on a straight line, and it would be difficult to determine $W-N$ for lead by extrapolating the general trend. Accordingly, we adopt another procedure, as follows. In Section III, we shall obtain the differences of the values of $W-N$ for radioactive elements from disintegration data. If we arbitrarily assign a $(W-N)$ value to the lead isotopes, higher than the correct one by an unknown amount, c, a knowledge of these differences makes it possible to plot $W-N+c$ as a function of N. The plotted points can be shifted up and down as a body, until a straight line representing their average trend passes through the plotted point for Hg^{200}. This line crosses the abscissa 206 at an ordinate of -0.008, so we take 205.992 ± 0.03 as a value of the isotopic weight of Pb^{206}. These relations are shown by the line marked XX' in Fig. 1. However, all the other data in this figure are plotted on the basis of the value 205.98 for the weight of Pb^{206}. This is a mean value obtained from all three methods outlined in this section. Accordingly, the $W-N$ values plotted for tungsten, rhenium, osmium, mercury and thallium are 0.004–0.012 or 0.008 lower than those obtained directly from packing fraction data, above.

(3) Our third method makes use of the relative abundances of the isotopes in ordinary and radioactive leads,[9] together with the atomic weights of these leads, determined chemically. Data are given in Table I. The assumption is made that the weights of these three isotopes differ by integers on the chemical scale, so that

[5] Aston, Nature **123**, 313 (1929).
[6] Aston, Nature **129**, 649 (1932).
[7] Aston, Proc. Roy. Soc. **A126**, 511 (1930); **132**, 487 (1931); **134**, 571 (1932).
[8] Hönigschmid, Birckenbach and Steinheil, Ber. **56B**, 1212 and 1219 (1923).
[9] Aston, Nature **120**, 224 (1927); **123**, 313 (1929); **129**, 649 (1932).

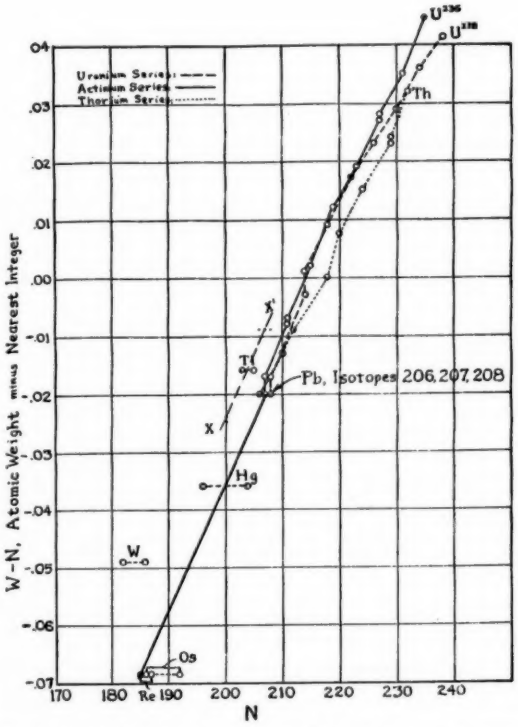

FIG. 1. Deviation of atomic weights of heavy elements from the nearest integer. Chemical scale, O = 16.0000.

they may be written $206+x$, $207+x$, and $208+x$, respectively.[10] We may use Wilberforce uraninite as an illustration. From Table I, $206.195 = 0.859(206+x)+0.83(207+x)+0.058(208+x)$. Then $x=-0.004$; that is, the calculated weight of Pb^{206} is 205.996.

On the basis of this assumption the four samples of lead in Table I yield the following values for the weight of Pb^{206}:

Material	*Isotopic weight of Pb^{206}*
Ordinary lead	206.030
Katanga pitchblende	205.981
Wilberforce uraninite	205.996
Norwegian thorite	206.005
Average	206.003±0.035

Weighting all three methods equally, the final mean for Pb^{206} is 205.987±0.03. Simultaneously with our announcement of the above results, a paper by von Grosse[11] appeared, in which he gives 205.96+0.02 as the weight of Pb^{206}. This is obtained from the data of Table I; the method of computation is not explained. We believe our mean is better supported *by the data above*, than the lower value of von Grosse. However, recent atomic weight determinations by Baxter and Alter[12] yield a *lower* value for Pb^{206} than any so far obtained. They have determined the atomic weight of lead extracted from a thorium-free cyrtolite occurring at Bedford, N. Y., with the result 205.924±0.02. An isotopic analysis of the Bedford material is much to be desired, for the discrepancy between this value and our mean may be due to the presence of the isotopes 203, 204, or 205, found by Aston.[13] Meanwhile, we shall give the cyrtolite value some weight by adopting the rounded value 205.98 for Pb^{206}. This mean depends on the results of three independent methods of attack, employing a number of atomic weight determinations, including Baxter and Bliss' work on Wilberforce lead, but it is quite possible that a lower value may be confirmed by later developments. If so, the effect will be to bring our calculated value for the atomic weight of radium (see Table II) into better agreement with the observed one; but the calculated and observed values for uranium will still disagree.

TABLE I. *Isotopic constitution of ordinary and radiogenic leads.*

Source of lead:	Ordinary lead	Katanga pitchblende	Wilberforce uraninite	Norwegian thorite
Chemical Atomic weight:	207.22[a]	206.048[b]	206.195[c]	207.90[d]
Percentage 206:	27.75	93.3	85.9	4.6
Percentage 207:	20.20	6.7	8.3	1.3
Percentage 208:	49.55	(0.02)	5.8	94.1
Other isotopes:	2.50	—	—	—

[a] International value.
[b] Hönigschmid and Birckenbach, Ber. **56**, 1837 (1923).
[c] Baxter and Bliss, J. Am. Chem. Soc. **52**, 4851 (1930).
[d] Fajans, Sitz. Heidelb. Akad. Wiss. **3** (1918); Hönigschmid, Phys. Zeits. **19**, 437 (1918); Zeits. f. Elektrochemie **25**, 91 (1919).

[10] Study of data on lighter elements indicates the degree to which this assumption may be trusted; the $(W-N)$ values determined by the mass-spectrograph for the isotopes of a single element never differ by more than 0.005 of a unit, and usually the departure is only 0.001 or 0.002. In the radioactive domain, however, the differences are larger, as we can see from Fig. 1. It appears likely that our assumption is correct within 0.01 of a unit of atomic weight. It should be considered merely as a convenient working hypothesis.

[11] von Grosse, Phys. Rev. **42**, 565 (1932).
[12] Baxter and Alter, Science **76**, 524 (1932).
[13] Aston, Nature **129**, 649 (1932).

III. Computation of the Isotopic Weights of Radioactive Substances

We shall now consider mass losses in disintegration. When an alpha-particle is emitted, two planetary electrons must leave the atom, so the atomic weight of a neutral helium atom plus the weight equivalent of the energy loss must be subtracted from the atomic weight of the parent atom to obtain that of the daughter. However, when a beta-particle is emitted, the planetary shells of the daughter atom pick up an electron. The only mass lost is that associated with the kinetic energy of the beta-particle and the energy of the gamma-rays.

In computing the energy loss in beta-ray transformations we use the average energy of the disintegration electrons rather than the maximum. It is well known that the average energy obtained with the beta-ray spectrograph is in agreement with the energy loss determined calorimetrically. The experimental facts require that we adopt one of several suppositions:

Either it is true that (1) energy is conserved only statistically in beta-ray transformations; or (2) an atom which sends out a slow disintegration electron must rid itself of surplus energy by the emission of penetrating rays or particles which are not detected in the calorimetric measurements or indeed in any others so far made; or (3) nuclei of a given species do not all have the same energy. Several other hypotheses, more or less complicated, might be mentioned. Our method of procedure corresponds to the first assumption, but if we were to use the maximum energy of the disintegration electrons, none of the atomic weights we calculate would be altered by more than a few thousandths. This is negligible in comparison with the uncertainty of 0.03 involved in the weights of the lead isotopes.

In the case of isotopes whose gamma-ray spectra are known, we have used the energy loss corresponding to the shortest gamma-ray recorded, in the hope that its energy is fairly close to the average surplus possessed by the excited nucleus just after disintegration. A detailed understanding of nuclear energy levels is not necessary for our purpose because the loss of energy by radiation corresponds in most cases to a negligible mass-loss. Where the spectrum is not known, we neglect the loss of energy by radiation. Inspection of known gamma-ray spectra shows that this procedure cannot possibly introduce an error greater than about 0.005 in any isotopic weight. Probably the average error thus introduced is closer to 0.001 unit.

The factors used in computation are these: Mass energy of atom having unit chemical atomic weight, $1.482\ 10^{-3}$ ergs, or $932\ 10^{6}$ electron-volts. One electron-volt corresponds to $1.074\ 10^{-9}$ chemical atomic weight units. Energies of alpha-particles, recoil atoms and beta-particles are taken from Gamow's[14] *Atomic Nuclei and Radioactivity*, with few exceptions. The data for U^{238}, U^{234}, and Th are those of Kurie, and of Kurie and Knopf,[15] while the values for U^{239} and U^{235} are assumed to be the same as those for U^{238} and U^{234}, respectively. For the hypothetical beta-rayers between U^{239} and U^{235}, we assume the disintegration electrons have the same energies as those of UX_1 and UX_2, respectively. A similar assumption is used in dealing with $MsTh_1$ and $MsTh_2$. No information is available concerning the gamma-rays of UY, Ac, An and AcA. We assume they are negligible.

Most of the gamma-ray energies were taken from *Radiations from Radioactive Substances*, by Rutherford, Chadwick and Ellis.[16] In a few cases it was necessary to estimate them from absorption coefficients given on page 456 of the same work, by use of the Klein-Nishina formula. The uncertainties thus introduced are negligible for our present purpose.

The results are shown in Table II.[17] The isotopic weights are given to a higher accuracy than the data warrant, to avoid error in rounding off. The outstanding facts which emerge from a study of these numbers are: (1) that in a gross

[14] Gamow, *Atomic Nuclei and Radioactivity*, pages 35 to 54, Oxford University Press.

[15] Kurie, Phys. Rev. **41**, 701 (1932); Kurie and Knopf, Phys. Rev. **43**, 311 (1933).

[16] Rutherford, Chadwick and Ellis, *Radiations from Radioactive Substances*, pp. 360–377, Cambridge University Press, 1930.

[17] Phys. Rev. **43**, 38–59 (1933) contains a group of papers by F. Allison and his associates, in which large numbers of new radioactive isotopes are proposed. These are fitted by Miss Bishop into four radioactive series. Independently Piggot proposes a somewhat similar arrangement. These schemes are highly hypothetical. We base our discussion on the disintegration sequences generally accepted.

TABLE II. *Mass losses and isotopic weights for the radioactive elements.* (*Chemical scale.*)

Isotope	Mass equivalent of energy loss: Alpha-particle and recoil atom	Beta-particle	Gamma-ray	Total mass loss	Isotopic weight
U^{238}	0.0044			0.0044+He	238.04
UX_1		0.0001		.0001	234.04
UX_2		.0004	0.00015	.00055	234.04
U^{234}	.0050			.0050+He	234.04
Io	.0050			.0050+He	230.03
Ra	.0052			.0052+He	226.02
Rn	.0059			.0059+He	222.02
Ra A	.0065			.0065+He	218.01
Ra B		.00025	.0005	.00075	214.00
Ra C		.0008	.0024	.0032	214.00
Ra C′	.0084			.0084+He	214.00
Ra D					209.99
Ra E		.0004		.0004	209.99
Ra F	.0058			.0058+He	209.99
Ra G					205.98
U^{239}?	.004(?)			.004+He	239.05
Beta-Rayer?		.0001(?)		.0001?	235.04
Beta-Rayer?		.0004(?)		.0004?	235.04
U^{235}	.005(?)			.005+He	235.04
UY					231.03
Pa	.0055		.0003	.0058+He	231.03
Ac					227.03
RdAc	.0065		.0007	.0072+He	227.03
AcX	.0062			.0062+He	223.02
An	.0075			.0075+He	219.01
Ac A	.0081			.0081+He	215.00
Ac B		.0002	.0005	.0007	210.99
Ac C	.0072		.0005	.0077+He	210.99
Ac C″		.0004	.0022	.0026	206.98
Ac D					206.98
Th	.0040			.0040+He	232.03
$MsTh_1$		.0001?		.0001	228.03
$MsTh_2$		.0004?	.0021	.0025	228.02
RdTh	.0058		.0001	.0059+He	228.02
ThX	.0062			.0062+He	224.02
Tn	.0068			.0068+He	220.00
Th A	.0073			.0073+He	216.00
Th B		.0001	.0003	.0004	211.99
Th C	.0066			.0066+He	211.99
Th C″		.0007	.0027	.0034	207.98
Th D					207.98

way, $W-N$ is a linear fraction of atomic weight for each radioactive series, and (2) that the mean rate of increase of $W-N$ with atomic weight is nearly the same for the three series. The equation $W-N=-0.02+0.00214(N-206)$ is a fair average representation of the atomic weights in the three series.

Isotopic weights of UI, Ra, Rn, and Ra F have also been computed by von Grosse,[18] whose results are 0.02 lower than ours.

The chemically-determined atomic weight of radium is 0.05 unit lower than our calculated value, and about 0.15 unit lower than the value obtained by calculation, on any reasonable basis, from the chemically-determined atomic weight of uranium. For thorium the discrepancy is 0.09 unit. In both cases the discrepancies are larger than the sum of the estimated uncertainties of the calculated and experimental values.

The value determined chemically for uranium is higher than one would expect on any assumption which appears probable in view of known facts. It can be understood if sufficient amounts of isotopes heavier than U^{238} are present, but Aston[19] found only the isotope U^{238}, and says, "uranium is probably simple to at

[18] von Grosse, Phys. Rev. **42**, 565 (1932).

[19] Aston, Nature **128**, 725 (1931).

least two or three percent." Wahlin[20] also found only a single isotope. It is possible, however, that several percent of U^{239} would have escaped detection in his experiment. If uranium were composed of the isotopes 238, 234 (in negligible amount), and 3 percent of 239, the atomic weight of the mixture calculated from our isotopic weights would be 238.07, which is 0.06 lower than the chemical value. Of course, small percentages of several higher isotopes would suffice to bring about agreement, but there is no positive evidence for their existence. As to U^{239}, we have summarized[21] the evidence on the origin of the actinium series, concluding that it is quite improbable that this isotope exists.

IV. Conclusions

Our conclusion is that the calculated values for the atomic weights of radium and thorium should be used in preference to those determined chemically, and that the accepted value for uranium appears too high on the basis of present information as to the isotopes of this element. In making this judgment, we wish to express admiration for the work of Hönigschmid and his collaborators on these atomic weights. In the case of uranium, for example, Hönigschmid and Schilz[22] made 37 determinations by several methods. For all three elements the inner consistency of the results leaves little to be desired, but it appears that systematic errors beyond the control of the chemist must have played a part. The only other possibilities are to assume that Einstein's energy-mass relation is not strictly valid or that energy is not even *statistically* conserved, in radioactive disintegration. Against both of these assumptions, a wealth of experimental evidence can be adduced.

[20] Wahlin, Phys. Rev. **39**, 183 (1932), and private communication.

[21] Western and Ruark, Phys. Rev. **43**, 205 (1933).

[22] Hönigschmid and Schilz, Z. anorg. chem. **170**, 145 (1928).

An Elementary Deduction of Gibbs' Adsorption Theorem

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The Gibbsian treatment of the thermodynamics of surfaces is very long and abstract. On the other hand the equations designated as "Gibbs' adsorption theorem" in all texts that have come to the authors' attention are only special cases, incompletely or inexactly derived, of the Gibbsian equation for constant temperature,

$$d\sigma = -\Sigma_{i=1}^{K}\Gamma_i d\mu_i.$$

An exact elementary deduction of this equation is therefore desirable. Such a deduction is given by means of a thermodynamic engine. Various closely related equations, all for constant temperature, are also deduced. The relation of the equations obtained to the most general Gibbsian equations, which include variations of temperature, is indicated. The assumptions underlying the Gibbsian treatment of the thermodynamics of surfaces are discussed briefly.

A. INTRODUCTION

THE term "Gibbs' adsorption theorem" has been rather indiscriminately applied to several more or less exact thermodynamic equations relating the surface tension and the adsorption at a surface layer to the concentrations, vapor pressures or chemical potentials of the components in the adjacent phase interiors. These equations may all be derived from the following general equation first given by Gibbs:[1]

$$d\sigma = -s^{\omega}dT - \sum_{i=1}^{K}\Gamma_i d\mu_i. \qquad (1)$$

σ is the surface tension, T the temperature, K the number of components of the system, μ_i the chemical potential (per mole) of the ith component, Γ_i is usually referred to either as the amount (in moles) of the ith component adsorbed per unit area of surface layer or the surface density of the ith component, and similarly s^{ω} is called the entropy per unit area of surface layer or the surface density of the entropy; the exact definition of the quantities Γ_i and s^{ω} is given below. For variations at constant temperature Eq. (1) becomes

$$d\sigma = -\sum_{i=1}^{K}\Gamma_i d\mu_i. \qquad (2)$$

It is this equation which in the present paper will be referred to as Gibbs' adsorption theorem.

Gibbs' deduction of Eq. (1) is very general and at the same time very exact. Another deduction both general and exact has been given by Defay.[2] Because of their completeness these treatments are so long and abstract that they have not been included in the standard texts on thermodynamics and on physical and colloid chemistry. The equations given in all texts that have come to the authors' attention are special cases of Eq. (2), incompletely or inexactly derived. It is the purpose of this paper to give an exact elementary deduction of Eq. (2) and some related equations. The deduction is carried out with the aid of the thermodynamic engine described below.

B. THE ENGINE

Let a system composed of two phases α and β separated by a plane surface layer ω (henceforth designated as the system $\alpha\beta\omega$) be contained in the thermodynamic engine indicated in Fig. 1. The surface layer ω, which is in general an inhomogeneous region of finite thickness, is represented by the shaded portion in Fig. 1. C is a geometrical surface whose significance is explained below. The material of the engine is supposed to be absolutely inert so that the properties of its contents remain unchanged

* National Research Fellow, 1933.

[1] J. W. Gibbs, *Collected Works*, Vol. I, p. 230, Eq. 508 (Longmans Green, 1928). The notation in the present paper differs somewhat from that of Gibbs.

[2] R. Defay, *Etude Thermodynamique de la Tension Superficielle, etc., I^re Partie*, reprinted from Bull. Acad. roy. Belg. (Classe des Sciences) 1929, 1930, 1931 (Hayez, Brussels 1931).

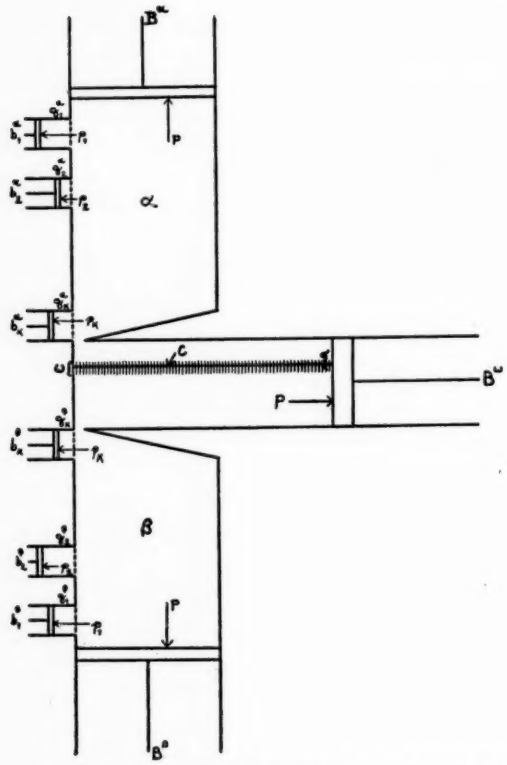


FIG. 1. Engine for demonstrating the thermodynamic laws of surface layers.

right up to the engine walls. B^α, B^β, B^ω are frictionless pistons. The cylinders q_1^α, $q_2^\alpha \cdots q_K^\alpha$ attached to the part of the engine containing the phase α contain the separate components of α in the pure state. Each pure component in its cylinder is separated from α by a membrane permeable only to that component. The part of the engine containing the phase β is similarly equipped with cylinders q_1^β, $q_2^\beta \cdots q_K^\beta$ containing the components of β in the pure state, separated from β by semipermeable membranes. If all K components of the system $\alpha\beta\omega$ are appreciably soluble in both phases, then there are K cylinders attached to each phase and the total number of the cylinders q_i^α, q_i^β is $2K$. But if some of the components are appreciably soluble in only one phase, the corresponding cylinders are omitted from the other phase, and the total number of the cylinders q_i^α, q_i^β is less than $2K$ by the number of components restricted to one phase only. By means of the frictionless pistons b_1^α, $b_2^\alpha \cdots b_K^\alpha$ and b_1^β, $b_2^\beta \cdots b_K^\beta$ the pure components may be reversibly added to or removed from the phases α and β respectively. The components in the cylinders q_i^α must therefore be in chemical equilibrium with the phase α and the components in q_i^β with the phase β, i.e., the pressures in q_i^α and q_i^β must be such that

$$\mu_i^{0\alpha} = \mu_i^\alpha \quad \text{and} \quad \mu_i^{0\beta} = \mu_i^\beta \quad (3.1), (3.2)$$

where $\mu_i^{0\alpha}$ and $\mu_i^{0\beta}$ denote the chemical potentials of the pure ith component in the cylinders q_i^α and q_i^β respectively, and μ_i^α and μ_i^β the chemical potentials in the phases α and β respectively. Finally it may be noted that the special case in which some of the components are practically insoluble in α and β but present in the surface layer ("insoluble surface film") may be treated by attaching cylinders q_i^ω (not shown in Fig. 1) for these components to the engine at such a level that their semipermeable membranes are in contact with ω. The condition for the chemical equilibrium between the pure component and the surface layer is then analogous to (3.1), (3.2), namely

$$\mu_i^{0\omega} = \mu_i^\omega. \quad (4)$$

C. The Definition of the Extensive Properties of the Surface Layer

Let C (Fig. 1) be a geometrical surface placed parallel to the surface layer at an arbitrary level with respect to the latter. C will henceforth be designated as the Gibbs surface. Let the two volumes into which the system $\alpha\beta\omega$ is divided by C be denoted by V^α and V^β respectively. Let G denote the value of any extensive property such as energy, entropy or the amount of a component for the system $\alpha\beta\omega$, and let g^α and g^β denote the value of the property in question per unit volume of the homogeneous phase interiors α and β. Then the quantity G^ω defined by the equations

$$G = G^\alpha + G^\beta + G^\omega \quad (5)$$

$$G^\alpha = g^\alpha V^\alpha, \quad G^\beta = g^\beta V^\beta \quad (6.1), (6.2)$$

is to be regarded as the energy, entropy, etc., of the *surface layer*. G^ω evidently represents the difference between the actual energy, entropy, etc., of the system $\alpha\beta\omega$ and that which it would have if α and β both remained homogeneous right up to the Gibbs surface C.

The extensive properties G^ω are evidently

proportional to the area of the Gibbs surface, which will be denoted by Ω. It is therefore expedient to define surface densities G^ω/Ω which correspond formally to the volume densities g^α, g^β in the phase interiors. Thus the surface densities of the entropy and of the ith component, appearing in Eq. (1) and designated by s^ω and Γ_i respectively, are defined by

$$s^\omega = S^\omega/\Omega, \quad \Gamma_i = n_i^\omega/\Omega \qquad (7.1), (7.2)$$

where S^ω is the surface entropy and n_i^ω is the number of moles of the ith component adsorbed at the surface.

Since the position of the Gibbs surface C is arbitrary, the quantities G^ω and their surface densities G^ω/Ω are not completely determined for a given state of the system $\alpha\beta\omega$ and a given value of Ω, but are functions of the position of C relative to the surface layer ω. The only G^ω and Γ_i values of physical interest, however, are those for which the Gibbs surface is placed within or very near the inhomogeneous region ω. Mathematically the position of the Gibbs surface relative to the surface layer may be fixed for each state of the system by adopting certain (arbitrary) conventions with respect to the values of Γ_i. A number of useful conventions of this kind have recently been proposed and the relations between them discussed in detail by Guggenheim and Adam.[3] Throughout the following discussion the *level of the Gibbs surface* and the *level of the surface layer* are taken to mean the respective levels *relative to the engine wall.*

Finally it is to be noted that since according to the above definitions the volume V of the system $\alpha\beta\omega$ is given by

$$V = V^\alpha + V^\beta \qquad (8)$$

the extensive quantity V^ω is necessarily zero and thus occupies a special position among the G^ω.

D. The Assumptions

The deductions given in this paper depend upon elementary principles and upon the five assumptions stated below. Of these assumptions only the last three are necessary for the validity of the equations deduced. The first two are made merely in order to simplify the working of the engine sufficiently; they thus indicate the extent to which the present deduction of Eq. (2) is less general than that of Gibbs.

1. The composition of the two phase interiors α and β and of the surface layer ω can be completely described in terms of the amounts (in moles) n_i^α, n_i^β, n_i^ω of *K electrically neutral* components

By the general method of Gibbs it can be shown that Eq. (2) holds also when the composition of the system must be described in terms of electrically charged components, if for each such component the electrochemical potential[4] is introduced in the same way as the chemical potential μ_i of an electrically neutral component. It may be noted that because of the electroneutrality of all phase interiors (at ordinary temperatures and pressures), assumption 1 is always fulfilled whenever the state of the surface layer is completely determined by the state of the two adjacent phase interiors. The simplest case in which it is not fulfilled is that in which one of the two phases is a conductor, the other a dielectric (e.g., NaCl solution|air) and the surface layer between them carries a net electric charge. Another case in which it is not fulfilled is that of the systems giving rise to electrocapillary curves elsewhere discussed by one of the authors.[5]

2. The surface layer is plane

By the general method of Gibbs it can be shown that Eq. (2) applies to curved as well as to plane surface layers under two conditions: (i) the radii of curvature of the surface layer are very large compared with its thickness; (ii) the Gibbs surface (whose position relative to a *plane surface layer* is *entirely* arbitrary) is placed within or very near the (curved) surface layer. There are no particular disadvantages connected with the latter restriction because, as already men-

[3] E. A. Guggenheim and N. K. Adam, Proc. Roy. Soc. A139, 218 (1933).

[4] On the concept of the electrochemical potential see E. A. Guggenheim, J. Phys. Chem. **33**, 842 (1929); **34**, 1540 (1930); *Modern Thermodynamics by the Methods of Willard Gibbs*, in print (Methuen, London, 1933).

[5] F. O. Koenig, J. Phys. Chem., in print; Wien-Harms, *Handbuch der Experimentalphysik.*, Vol. XII, Part 2, in print (Akademische Verlagsgesellschaft m.b.H. Leipzig).

tioned, the only G^ω and Γ_i values of physical interest are those for which the Gibbs surface is placed within or very near the surface layer anyway. If the radii of the surface layer become of the same order as its thickness, then the whole problem becomes more complicated and Eq. (2) is no longer applicable.

3. Macroscopic electric, magnetic and gravitational fields are absent or of negligible influence

In the absence of gravity the pressure and composition of any phase interior are constant throughout all its parts. In a gravitational field the pressure and composition are functions of the gravitation potential, i.e., they are variable in the direction of the field. In the earth's field however the effect of this variation on the values of surface tension σ, chemical potential μ_i and adsorption Γ_i in the systems usually studied is entirely negligible. Consequently any theoretical result connecting the quantities σ, μ_i, Γ_i (Eq. (2)) and obtained on the assumption that gravity is absent is also valid in gravitational fields of terrestrial magnitude.

4. The first and second laws of thermodynamics

These laws are used in the form of the theorem that in any isothermal process the gain in the Helmholtz free energy of a system is equal to the total reversible work done on the system in the process. They are also implied in the equilibrium conditions stated below (assumption 5).

5. The system $\alpha\beta\omega$ is in thermal, mechanical and chemical equilibrium

The condition for thermal equilibrium is that the temperature T be the same throughout the system.

The condition for the mechanical equilibrium of two phases separated by a plane boundary layer (assumption 2) in the absence of gravity (assumption 3) is that the pressures P^α and P^β in the two phase interiors be equal, i.e.,

$$P^\alpha = P^\beta = P. \tag{9}$$

The condition for chemical equilibrium is that for each electrically neutral component (assumption 1) appreciably soluble in both phases, the chemical potentials μ_i^α and μ_i^β in the two phase interiors be equal, i.e.,

$$\mu_i^\alpha = \mu_i^\beta = \mu_i. \tag{10}$$

From this equation and (3.1), (3.2) it follows that for any component soluble in both α and β, the chemical potentials in the corresponding cylinders q_i^σ, q_i^β are also equal, i.e.,

$$\mu_i^{0\alpha} = \mu_i^{0\beta} = \mu_i^0 = \mu_i \tag{11}$$

and hence that the pressures p_i^α, p_i^β in the cylinders q_i^α, q_i^β are equal, i.e.,

$$p_i^\alpha = p_i^\beta = p_i. \tag{12}$$

For any component, say the hth, soluble only in α and not in β or *vice versa*, the upper suffix α or β may without loss of generality be omitted in all following formulas and the notation of Eqs. (11), (12) preserved by writing:

$$\mu_h^{0\alpha} = \mu_h^0 = \mu_h \quad \text{or} \quad \mu_h^{0\beta} = \mu_h^0 = \mu_h \quad (13.1), (13.2)$$

$$p_h^\alpha = p_h \quad \text{or} \quad p_h^\beta = p_h. \quad (14.1), (14.2)$$

The same convention is applicable also to the case in which some of the components are soluble only in the surface layer (insoluble surface film, Eq. (4)), so that for any such component, say the jth,

$$\mu_j^{0\omega} = \mu_j^0 = \mu_j \tag{15}$$

$$p_j^\omega = p_j. \tag{16}$$

E. The Deduction of Eq. (2)

Eq. (2) may be deduced by carrying out the following two processes with the engine, equating the gain in the Helmholtz free energy (abbreviated Hfe.) of the *entire engine* (i.e., of the system $\alpha\beta\omega$+the cylinders q_i^α, q_i^β (and q_i^ω)) to the total work done on the entire engine in each process and combining the resulting equations.

Process 1

By moving the pistons B^α, B^β, B^ω and the level of the Gibbs surface C infinitesimally, change V^α, V^β and Ω by arbitrary infinitesimal amounts, dV^α, dV^β, $d\Omega$, simultaneously moving the pistons b_i^α, b_i^β (and b_i^ω in the case of insoluble surface films so as to change the number of moles n_i of the components in $\alpha\beta\omega$ by arbitrary infinitesimal amounts dn_i.

The gain in the Hfe. of the entire engine in

this process may be calculated as follows. From Eq. (5) it follows that the gain dA in the Hfe. of the system $\alpha\beta\omega$ in any infinitesimal process whatever is given by

$$dA = dA^\alpha + dA^\beta + dA^\omega. \tag{17}$$

The gain in the Hfe. of the cylinders q_i^α, q_i^β (and q_i^ω) is evidently equal to

$$-\sum_{i=1}^{K} \mathrm{A}_i^0 dn_i \tag{18}$$

where A_i^0 is the molal Hfe. of the ith pure component at T, p_i and dn_i represents the amount of the component transferred from both cylinders q_i^α and q_i^β (or from q_i^ω) to the system $\alpha\beta\omega$. The gain in the Hfe. of the entire engine is therefore

$$dA^\alpha + dA^\beta + dA^\omega - \sum_{i=1}^{K} \mathrm{A}_i^0 dn_i. \tag{19}$$

The work done by the entire engine consists of the volume work done by B^α, B^β, B^ω:

$$-P dV^\alpha - P dV^\beta \tag{20}$$

the surface work done by B^ω:

$$\sigma d\Omega \tag{21}$$

and the volume work done by b_i^α, b_i^β (b_i^ω):

$$\sum_{i=1}^{K} p_{ii} \mathrm{V}^0 dn_i \tag{22}$$

where V_i^0 denotes the molal volume of the pure ith component at T, p_i. Hence for process 1

$$dA^\alpha + dA^\beta + dA^\omega - \sum_{i=1}^{K} \mathrm{A}_i^0 dn_i$$

$$= -P dV^\alpha - P dV^\beta + \sigma d\Omega + \sum_{i=1}^{K} p_i \mathrm{V}_i^0 dn_i \tag{23}$$

$$dA^\alpha + dA^\beta + dA^\omega = -P dV^\alpha - P dV^\beta + \sigma d\Omega$$

$$+ \sum_{i=1}^{K} (\mathrm{A}_i^0 + p_i \mathrm{V}_i^0) dn_i. \tag{24}$$

A_i^0 is related to the Gibbs free energy F_i^0 per mole of pure component by

$$\mathrm{A}_i^0 + p_i \mathrm{V}_i^0 = \mathrm{F}_i^0 \tag{25}$$

and F_i^0 is in turn equal to the chemical potential μ_i^0. Hence by Eqs. (11), (13), (15),

$$\mathrm{A}_i^0 + p_i \mathrm{V}_i^0 = \mu_i \tag{26}$$

so that *Eq.* (24) becomes

$$dA^\alpha + dA^\beta + dA^\omega = -P dV^\alpha - P dV^\beta + \sigma d\Omega$$

$$+ \sum_{i=1}^{K} \mu_i dn_i. \tag{27}$$

Since by Eq. (5)

$$dn_i = dn_i^\alpha + dn_i^\beta + dn_i^\omega \tag{28}$$

Eq. (27) becomes

$$dA^\alpha + dA^\beta + dA^\omega = -P dV^\alpha - P dV^\beta + \sigma d\Omega$$

$$+ \sum_{i=1}^{K} \mu_i dn_i^\alpha + \sum_{i=1}^{K} \mu_i dn_i^\beta + \sum_{i=1}^{K} \mu_i dn_i^\omega. \tag{29}$$

The state of the system $\alpha\beta\omega$ is completely determined by the temperature T, the volume $V(= V^\alpha + V^\beta)$, the area Ω and the number of moles $n_i(= n_i^\alpha + n_i^\beta + n_i^\omega)$ of the components. In process 1 all of these quantities except T have been varied in an arbitrary way. Hence Eq. (29) applies to any isothermal change whatever to which the system $\alpha\beta\omega$ in equilibrium can be subjected.

Process 2

Imagine the piston B^ω to have been pushed as far to the left (Fig. 1) as possible, so that Ω is zero and the phases α and β are isolated mechanically and chemically. Then by moving the pistons B^α and b_i^α change V^α and n_i^α by arbitrary infinitesimal amounts dV^α and dn_i^α.

The gain in the Hfe. of the entire engine in this process is

$$dA^\alpha - \sum_{i=1}^{K} \mathrm{A}_i^0 dn_i^\alpha \tag{30}$$

and the work done on the entire engine is

$$-P dV^\alpha + \sum_{i=1}^{K} p_i \mathrm{V}_i^0 dn_i^\alpha. \tag{31}$$

Hence

$$dA^\alpha - \sum_{i=1}^{K} \mathrm{A}_i^0 dn_i^\alpha = -P dV^\alpha + \sum_{i=1}^{K} p_i \mathrm{V}_i^0 dn_i^\alpha \tag{32}$$

$$dA^\alpha = -P dV^\alpha + \sum_{i=1}^{K} (\mathrm{A}_i^0 + p_i \mathrm{V}_i^0) dn_i^\alpha \tag{33}$$

and, by Eq. (26),

$$dA^\alpha = -P dV^\alpha + \sum_{i=1}^{K} \mu_i dn_i^\alpha. \tag{34.1}$$

The state of any phase α is completely determined by the temperature T, the volume V^α and the number of moles n_i^α of the components. In process 2 all of these quantities except T have been varied in an arbitrary way. Hence Eq. (34.1) applies to any isothermal change whatever to which the phase α in equilibrium can be subjected. The corresponding equation for the phase β is evidently

$$dA^\beta = -PdV^\beta + \sum_{i=1}^{K} \mu_i dn_i^\beta. \qquad (34.2)$$

Combination of the equations resulting from processes 1 and 2

Since Eqs. (29), (34.1), (34.2) are perfectly general for any infinitesimal isothermal change in which equilibrium is preserved, the subtraction of (34.1) and (34.2) (derived by process 2) from (29) (derived by process 1) leaves

$$dA^\omega = \sigma d\Omega + \sum_{i=1}^{K} \mu_i dn_i^\omega \qquad (35)$$

and this equation must also hold for any infinitesimal isothermal change to which the system $\alpha\beta\omega$ in equilibrium can be subjected.

For a given state of the system $\alpha\beta\omega$ the intensive quantities in Eq. (35) are fixed, but Ω is still variable, and the extensive quantities A^ω, n_i^ω are proportional to Ω for a given position of the Gibbs surface relative to the surface layer. Consequently Eq. (35) may be integrated, keeping the intensive quantities and the position of the Gibbs surface relative to the surface layer constant, and allowing Ω to vary, the result is

$$A^\omega = \sigma\Omega + \sum_{i=1}^{K} \mu_i n_i^\omega + \Phi \qquad (36)$$

where the integration constant Φ is a function of T, σ, μ_i and the position of the Gibbs surface relative to the surface layer. When Ω is zero, A^ω and n_i^ω are also zero and therefore Φ is zero, leaving as the complete expression for the Hfe. of the surface layer

$$A^\omega = \sigma\Omega + \sum_{i=1}^{K} \mu_i n_i^\omega. \qquad (37)$$

The differentiation of (37) gives

$$dA^\omega = \sigma d\Omega + \Omega d\sigma + \sum_{i=1}^{K} \mu_i dn_i^\omega + \sum_{i=1}^{K} n_i^\omega d\mu_i. \qquad (38)$$

This equation applies to any infinitesimal change whatever, and therefore in particular to the general isothermal change to which Eq. (35) refers. Consequently the subtraction of (35) from (38) gives

$$0 = \Omega d\sigma + \sum_{i=1}^{K} n_i^\omega d\mu_i \qquad (39)$$

which, like (35), holds for any infinitesimal isothermal change in which equilibrium is preserved. Solving (39) for $d\sigma$ and taking account of Eq. (7.2) gives Gibbs' adsorption theorem, Eq. (2):

$$d\sigma = -\sum_{i=1}^{K} \Gamma_i d\mu_i. \qquad (2)$$

F. Some Further Equations Directly Derivable from the Engine

The important relation (35) was obtained by a mathematical operation carried out upon Eqs. (29), (34.1), (34.2) which were directly derived from the engine. It is perhaps worth while indicating how some of the consequences of (35) can be obtained directly from the engine.

Thus it is possible to examine the effect of a change in the relative positions of the Gibbs surface and the surface layer, the state of the system and Ω remaining constant. For this change (35) gives

$$dA^\omega = \sum_{i=1}^{K} \mu_i dn_i^\omega \qquad (40)$$

which, since the μ_i are constant, may be integrated, giving for a finite shift of the Gibbs surface relative to the surface layer

$$\Delta A^\omega = \sum_{i=1}^{K} \mu_i \Delta n_i^\omega. \qquad (41)$$

Each of the Eqs. (40), (41) is directly derivable from the engine. To derive (40) it is only necessary to shift the level of the surface layer infinitesimally with respect to the engine wall, the level of the Gibbs surface with respect to the engine wall, V^α, V^β, Ω and all intensive variables being kept constant. This can be done by keeping B^α, B^β, B^ω stationary and operating

b_i^α, b_i^β so as to add to one of the phases, say α, its components in the proportions in which they are present in the interior of α, simultaneously removing from β its components in the proportions in which they are present in the interior of β, the amounts added to α and removed from β being such that P remains constant. From Eqs. (5), (6.1), (6.2) it follows that for any infinitesimal change whatever

$$dG = d(g^\alpha V^\alpha) + d(g^\beta V^\beta) + dG^\omega. \tag{42}$$

Since in the change in question V^α, V^β and the intensive variables g^α, g^β remain constant,

$$dG = dG^\omega \tag{43}$$

so that in particular

$$dA = dA^\omega \tag{44}$$

$$dn_i = dn_i^\omega. \tag{45}$$

The gain in the Hfe. of the entire engine is therefore

$$dA^\omega - \sum_{i=1}^{K} \mathrm{A}_i^0 dn_i^\omega \tag{46}$$

and the work done on the entire engine is

$$\sum_{i=1}^{K} p_i \mathrm{V}_i^0 dn_i^\omega. \tag{47}$$

Hence

$$dA^\omega - \sum_{i=1}^{K} \mathrm{A}_i^0 dn_i^\omega = \sum_{i=1}^{K} p_i \mathrm{V}_i^0 dn_i^\omega \tag{48}$$

which by Eq. (26) leads directly to (40). To obtain (41) the process is made finite instead of infinitesimal and the operator d in the formulas (42)–(48) replaced by Δ.

Another important relation directly derivable from the engine is Eq. (37). For this purpose cause B^ω to generate the finite surface area Ω, simultaneously moving B^α, B^β, B^ω, b_i^α, b_i^β (and b_i^ω in the case of insoluble surface films, in such a way as to keep all intensive variables, the volumes V^α, V^β, the level of the Gibbs surface and the level of the surface layer constant. This process is best carried out in four steps: (i) generation of Ω by B^ω, whereby V^α, V^β, P and the concentrations c_i^α, c_i^β are changed; (ii) restoration of V^α and V^β to their original values by B^α and B^β respectively; (iii) restoration of c_i^α, c_i^β (and the surface densities of any components present only in the surface layer) and therefore P to their original values by means of b_i^α, b_i^β (and b_i^ω); (iv) restoration of the surface layer to its original level by means of b_i^α, b_i^β as in the foregoing derivation of Eq. (40). From Eq. (42) it follows that for any finite change

$$\Delta G = \Delta(g^\alpha V^\alpha) + \Delta(g^\beta V^\beta) + \Delta G^\omega. \tag{49}$$

Since in the change in question V^α, V^β and all intensive variables remain constant and the surface Ω is generated,

$$\Delta G = \Delta G^\omega = G^\omega \tag{50}$$

so that in particular

$$\Delta A = A^\omega \tag{51}$$

$$\Delta n_i = n_i^\omega \tag{52}$$

where Δn_i is the total amount of the ith component added to or removed from the system $\alpha\beta\omega$ in steps (iii) and (iv) above. The gain in the Hfe. of the entire engine is therefore

$$A^\omega - \sum_{i=1}^{K} \mathrm{A}_i^0 n_i^\omega \tag{53}$$

and the work done on the entire engine is

$$\sigma\Omega + \sum_{i=1}^{K} p_i \mathrm{V}_i^0 n_i^\omega. \tag{54}$$

Hence

$$A^\omega - \sum_{i=1}^{K} \mathrm{A}_i^0 n_i^\omega = \sigma\Omega + \sum p_i \mathrm{V}_i^0 n_i^\omega \tag{55}$$

which by Eq. (26) leads directly to (37).

It may furthermore be noted that just as Eq. (35) for a surface layer was integrated to give Eq. (37), so may Eq. (34.1) for a single phase α be integrated keeping all intensive variables constant and allowing only V^α to vary; the result is

$$A^\alpha = -PV^\alpha + \sum_{i=1}^{K} \mu_i n_i^\alpha. \tag{56}$$

This equation, like (37), may also be derived directly from the engine by making process 2 above finite and keeping all intensive variables constant. Finally, Eq. (29) may be integrated in a manner similar to Eqs. (35) and (34.1), (or (34.2)); the result is the complete

expression for the Hfe. of the system $\alpha\beta\omega$:

$$A = A^\alpha + A^\beta + A^\omega = -PV^\alpha - PV^\beta + \sigma\Omega + \sum_{i=1}^{K} \mu_i n_i^\alpha + \sum_{i=1}^{K} \mu_i n_i^\beta + \sum_{i=1}^{K} \mu_i n_i^\omega \quad (57)$$

$$= -PV + \sigma\Omega + \sum_{i=1}^{K} \mu_i n_i \quad (58)$$

and these equations too are immediately obtainable from the engine by allowing it to generate the whole system $\alpha\beta\omega$ keeping the intensive variables constant. Eqs. (57), (58) are of course also obtainable by combining (37) with (56) and with the integrated form of (34.2).

G. Comparison of the Equations Derived from the Engine with the General Gibbsian Equations

The differential equations for the Hfe. derived in this paper apply only to isothermal changes, but are otherwise quite general for the cases defined by the above assumptions 1 and 2. It therefore seems worth while comparing these equations with the completely general equations which take account of changes of temperature. The latter equations, obtainable by the method of Gibbs, differ from the isothermal equations only by an additive term of the form SdT. Thus the general equation corresponding to (29) is

$$dA^\alpha + dA^\beta + dA^\omega = -S^\alpha dT - S^\beta dT - S^\omega dT - PdV^\alpha - PdV^\beta + \sigma d\Omega + \sum_{i=1}^{K} \mu_i dn_i^\alpha + \sum_{i=1}^{K} \mu_i dn_i^\beta + \sum_{i=1}^{K} \mu_i dn_i^\omega \quad (59)$$

or, more compactly,

$$dA = -SdT - PdV + \sigma d\Omega + \sum_{i=1}^{K} \mu_i dn_i. \quad (60)$$

The general equation corresponding to (35) is:

$$dA^\omega = -S^\omega dT + \sigma d\Omega + \sum_{i=1}^{K} \mu_i dn_i^\omega \quad (61)$$

and to (34.1):

$$dA^\alpha = -S^\alpha dT - PdV^\alpha + \sum_{i=1}^{K} \mu_i dn_i^\alpha. \quad (62)$$

It is worth noting that the integration of the general Eqs. (59), (60), (61), (62) keeping all intensive variables constant leads to Eqs. (57), (58), (37), (56) already obtained in this paper; the integrated equations derived from the engine therefore do not suffer from the fact that the corresponding differential equations apply only to isothermal changes.

Finally, just as the combination of (37) with the isothermal equation (35) leads to the isothermal Eq. (2), so does the combination of (37) with the general Eq. (61) lead to the general Eq. (1).

H. Summary

An exact elementary deduction of Gibbs' adsorption theorem,

$$d\sigma = -\sum_{i=1}^{K} \Gamma_i d\mu_i \quad (2)$$

and some related equations is given by means of a suitable thermodynamic engine. The assumptions underlying the Gibbsian treatment of the thermodynamics of surfaces are discussed briefly. The relation of the equations derived to the corresponding general Gibbsian equations is explained.

A Calculation of the Equilibria in Keto-Enol Tautomerism

G. W. WHELAND, *Gates Chemical Laboratory, California Institute of Technology**

(Received July 20, 1933)

A calculation of the equilibria obtaining in some simple cases of keto-enol tautomerism has been carried through with the aid of bond and resonance energies derived from empirical data. The results obtained are in qualitative and semi-quantitative agreement with experiment.

THE energy of a molecule which can be represented by a single Lewis electronic structure is given with considerable accuracy by the sum of the energies of the various bonds which it contains. On the other hand, the energy of a molecule which can be represented adequately only in terms of two or more structures is, as a result of resonance, greater than would be predicted for even the stablest of them, on the basis of bond energies alone. The amount of this extra energy has been calculated from empirical data by Pauling and Sherman[1] for a number of cases, and has been shown to be fairly constant for a given type of resonance. We can, consequently, calculate the energy of an arbitrary molecule if we know the energy of each of its bonds and in addition the contribution made by any resonating systems that may be present.[2] Unfortunately, however, we do not have sufficient accurate data of this kind to proceed very far except in a few simple cases, and so we must usually resort to rough estimates and content ourselves with general results of a more or less qualitative nature. The purpose of the present paper is to apply this type of treatment to the problem of keto-enol tautomerism. The results obtained are quite satisfactory qualitatively and semi-quantitatively, and are of such nature as to lead one to expect that a more rigorous treatment would give complete agreement with experiment. Since, however, this will have to wait until more powerful methods than are now available have been developed, it seems of interest in the meantime to carry the rougher and more qualitative methods as far as possible.

The calculations are simplified to a certain extent by the fact that the entropy change in the reaction keto→enol is apparently very small.[3] We can consequently neglect it entirely and put $\Delta H = \Delta F$. This is convenient since it makes possible a direct comparison between the values of ΔH given by the calculation and the values of ΔF derived from experimental data. In only a few cases are experimental ΔH values known.

Simple Keto-Enol System

I II

In the keto grouping I there is no possibility of resonance, and so the energy is simply the sum of the bond energies. This amounts to 357.2 Cal. if the C=O group is aldehydic, and to 360.6 Cal. if it is ketonic. In the enol grouping II, resonance between the two structures

is possible, but presumably the second structure does not make a very large contribution and the resonance energy is small. That some resonance does occur, however, is made probable by the

* Communication No. 373.

[1] L. Pauling and J. Sherman, J. Chem. Phys. **1**, 606 (1933). All bond and resonance energies given without reference will be taken from this paper.

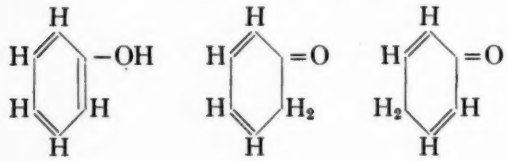
[2] This is rather an over-simplification since it leaves out of account the energy resulting from interaction between the dipoles in the molecule. This effect is usually small, and so we shall neglect it in the following discussion, except in a few cases where it becomes of special importance.

[3] J. B. Conant and A. F. Thompson, Jr., J. Am. Chem. Soc. **54**, 4039 (1932). Most of the data regarding the equilibria with β-diketones and β-ketonic esters are taken from this paper.

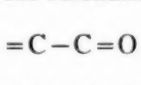
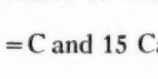
fact that the enols are considerably stronger acids than the alcohols. The bond energy for the enol grouping is 339.9 Cal. if the energy of the C–O bond is the same as for primary alcohols. Actually it is probably somewhat higher since an enol bears a rather closer resemblance to a secondary or tertiary than to a primary alcohol. The total energy of the enol grouping is then slightly greater than 339.9 Cal.—probably about 346.8 Cal. since in phenol similar effects raise the energy by 6.9 Cal. Thus ketones should be approximately 14 Cal. and aldehydes 10 Cal. more stable than the corresponding enols. This is in qualitative agreement with experiment; since the enols of this type are too unstable ever to have been isolated, a quantitative comparison cannot be made.

Phenol

One enolic and two ketonic forms are possible.

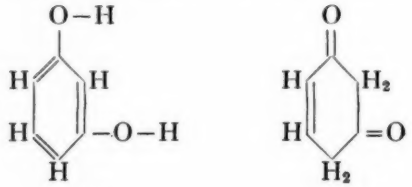


III IV V

(In the structure III the benzene ring is written, for the sake of convenience, as if it possessed the simple Kekulé form. Actually, of course, it resonates among several structures, of which this is only one.[4]) As far as the keto and enol groupings are concerned, the two keto forms IV and V should be more stable than the enol III by 14 Cal. The resonance energy remains to be considered, however. For the enol form this amounts to 39 Cal. (resonance within the benzene ring), and for the two keto forms to considerably less, probably between 13 and 19 Cal. The reason for this is as follows. The resonance energy of the system C=C–C=C can be calculated by the method described by Pauling and Wheland, and is found to be approximately 8 Cal. The resonance energy of the system C=C–C=O is probably a little less than 10 Cal.[5]—that is to say, practically the same as for C=C–C=C. Consequently it seems reasonable to assume that the resonance energies of the systems C=C–C=C–C=O and  lie close to the values 17 Cal. calculated for C=C–C=C–C=C and 15 Cal. calculated for  , respectively. It follows then that the enol form of phenol is more stable than either of the keto forms by 6–12 Cal. Again the agreement with experiment is qualitatively satisfactory, but a quantitative comparison is impossible on account of lack of experimental data.

Resorcinol

There is one dienolic and one diketonic form.

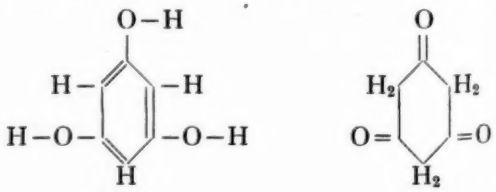


VI VII

(The intermediate keto-enolic forms turn out to be less stable than either of the above.) If the resonance energy is neglected the diketonic form VII would be expected to be more stable than the dienolic VI by about 28 Cal. When the 39 Cal. resonance energy for the benzene ring and the 10 Cal. for the system C=C–C=O are considered, however, the dienol becomes more stable by 1 Cal. This is in qualitative agreement with the fact that resorcinol shows more of a ketonic behavior than phenol, but that its phenolic character is still predominant.

Phloroglucinol

There is one trienolic and one triketonic form.



VIII IX

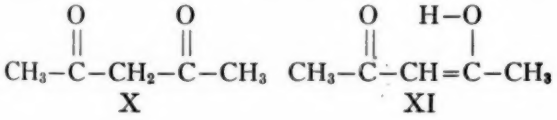
[4] L. Pauling and G. W. Wheland, J. Chem. Phys. 1, 362 (1933).

[5] This value is derived from data quoted by W. Hückel, *Theoretische Grundlagen der Organischen Chemie*, Vol. I, p. 304, Leipzig, 1931, regarding the heats of combustion of isomeric $\alpha\beta$ and $\beta\gamma$ unsaturated ketones.

A calculation similar to the above gives the result that the triketonic form IX should be 3 Cal. more stable than the trienolic form VIII. This is again in good qualitative agreement with the fact that phloroglucinol possesses both phenolic and ketonic character, but the quantitative aspect is less satisfactory, as the phenolic character is apparently still predominant. The agreement would have been somewhat better if the dipole interactions had been considered. No great weight should be attached to the actual numerical values derived in this and the preceding calculations as they could hardly be expected to be accurate within a few kilocalories. The relative values, however, are probably significant.

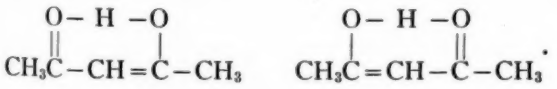
Acetylacetone

This is chosen as a typical example of a β-diketone. The keto and the enol forms (X and XI, respectively) are both known, and the free energy change accompanying the conversion of



X XI

the keto into the enol form has been found to be -1 Cal. With compounds of this type an additional complication enters in the fact that the enolic modification does not have the simple structure given above, but contains a chelate ring with a hydrogen bond. The resulting compound is then free to resonate between the two equivalent structures:

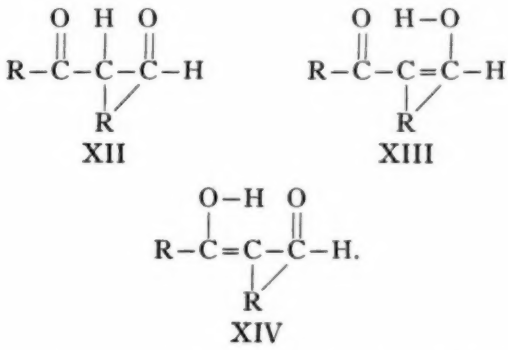


The amount by which this bond formation and resonance stabilizes the enol form can be calculated from the fact mentioned above that ΔF for the reaction keto$\rightarrow$enol is -1 Cal. The keto form is readily seen to be 4 Cal. more stable than the open-chain enol form, and hence the formation of the chelate ring must stabilize the latter by an additional 5 Cal. This value is reasonable enough, but unfortunately cannot be checked by an independent calculation.

There is no provision in this treatment for the effect of substituent groups in the molecule (provided that at least one enolizable hydrogen is left), and in fact the calculation leads to the conclusion that the enolization should be independent of the presence of substituents. Actually this is not the case, but the effect of substitution is very small—less than 2 Cal. in all cases—and lies well within the accuracy of the method.

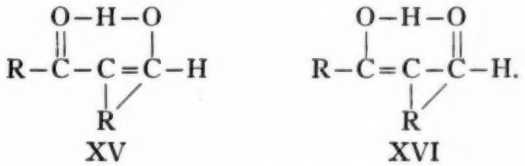
Oxymethylene Ketones or β-Ketonic Aldehydes

In compounds of this type enolization can take place in either of two ways and consequently there are (before formation of the chelate ring) two enol forms (XIII and XIV) in addition to the one keto form XII.



XII XIII XIV

Since the energy of the C=O bond in aldehydes is 3.4 Cal. less than in ketones, it follows that the stability of the enol XIII is greater than that of XIV and nearly as great as that of the keto form XII. When the hydrogen bond is formed the resonance in the chelate ring will be less than in the case of the diketones as a result of the non-equivalence of the two structures



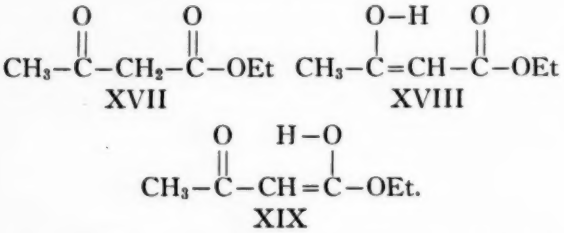
XV XVI

The effect of this will be twofold. In the first place, the energy of the ring will be less than 5 Cal., but probably still enough to make the enol form more stable than the keto; and in the second place, the structure XV will predominate over XVI since it represents the more stable

configuration. Experimentally, compounds of this type (for example, oxymethylene camphor) are found to possess the oxymethylene ketone structure, corresponding to the enol XIII or XV, in qualitative confirmation of the calculation. There are no accurate experimental data of quantitative nature for purpose of comparison.

Acetoacetic Ester

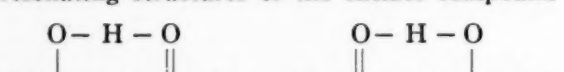
A β-ketonic ester can give rise to two (open-chain) enolic modifications (XVIII and XIX) in addition to the ketonic (XVII).



XVII XVIII

XIX

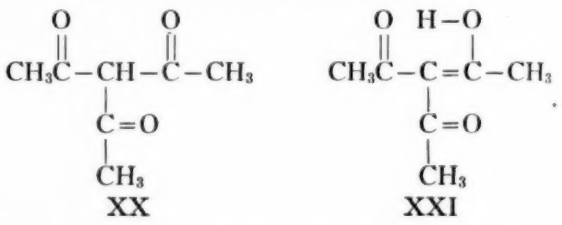
This problem is complicated by the fact that the carbethoxy group has a resonance of its own which makes the relatively large contribution of 28 Cal. to the energy of the molecule, and that this resonance is interfered with to an uncertain extent by any other types of resonance that may be present. In the keto form this effect does not enter since there is no other resonance than that of the carbethoxy group. In the enol form XVIII it is apparently of very minor importance since in a few cases for which data are available[6] the resonance energy of $\alpha\beta$ unsaturated acids is essentially the same as if the C=C−C=O and the carboxyl groups were entirely independent of each other. In the enol form XIX, however, the carbethoxy group and its resonance energy have been destroyed, and hence this structure represents a relatively unstable molecule. The conclusions to be drawn from these considerations are: first, that the β-ketonic esters should be somewhat less enolic than the β-diketones, as a result mainly of damping of resonance in the chelate ring; and second, that the first of the resonating structures of the chelate compound



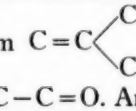
should predominate over the second. Both conclusions are in agreement with experiment. Acetoacetic ester is less enolic than acetyl acetone by about 1 Cal. (ΔF=O Cal.), and the position of the C=C double bond has been determined by ozonization.[7] The β-ketonic esters are perhaps somewhat more enolic than might be expected from the discussion, but the agreement with the calculation is really quite satisfactory.

Triacetylmethane

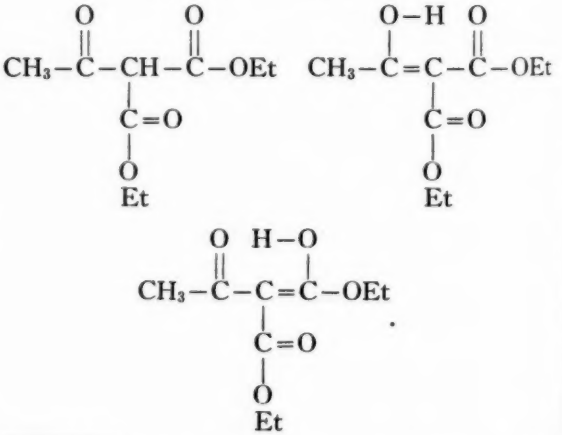
In this case there is only one keto and one enol form (XX and XXI, respectively).



XX XXI

We see that this compound will be more enolic than acetylacetone by the amount by which the resonance of the system  exceeds that of the system C=C−C=O. An estimate of about 4–8 Cal. seems to be reasonable for this figure and to agree satisfactorily with what little experimental data there are. The compound is usually considered to be completely enolic, but the equilibrium has never been measured accurately.

Acetylmalonic Ester

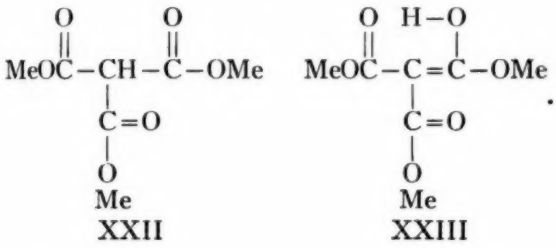


[6] For example, the heats of combustion of $\alpha\beta$ and $\beta\gamma$-pentenoic acids differ by 8.5 Cal. See M. S. Kharasch, Bur. Standards J. Research **2**, 359 (1929).

[7] J. Scheiber and P. Herold, Ann. d. Chemie **405**, 295 (1914).

This compound would be expected to be less enolic than triacetylmethane (for the same reason that acetoacetic ester is less enolic than acetylacetone) and to be more enolic than acetoacetic ester. Experimentally, ΔF of enolization is found to be about -0.5 Cal. A value between -4 and -8 Cal. would seem more reasonable, but the qualitative agreement is good.

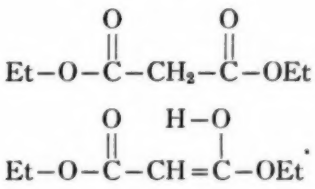
TRICARBOMETHOXY METHANE

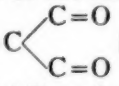


XXII XXIII

The stability of the enol form XXIII is decreased very materially by the fact that in it one of the carbomethoxy groups is no longer intact. Just how great this effect will be, however, cannot be predicted with any assurance since, as a result of the resonance within the chelate ring, the relationships involved are very complicated. All that can be said definitely is that this compound should be less enolic than acetylmalonic ester. This is indeed the case, but the difference is very much less than might be expected. The enolic form is less stable than the ketonic by only about 1 Cal., while a value of 10–20 Cal. would seem more reasonable. The quantitative aspects of the present treatment are consequently very unsatisfactory at this point, although the qualitative agreement is still good. Two possible explanations for this discrepancy suggest themselves at once. In the first place, the value of 28 Cal. for the resonance energy of the carbomethoxy group may be considerably too high. This figure was arrived at[1] on the doubtful assumption that the energies of the C=O and the C–O bonds were the same as in ketones and primary alcohols, respectively, and consequently may very well be in error by several kilocalories. In the second place, the neglect of the large interaction between the dipoles in the carbomethoxy group is probably not legitimate.

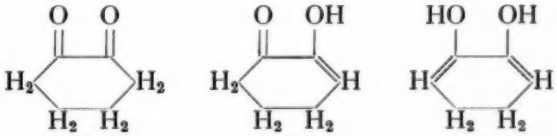
MALONIC ESTER



This case differs from the preceding only in the substitution of the resonating system C=C–C=O for  in the enol form. Consequently the stability of the enol relative to that of the keto should be decreased by the difference between the resonance energies of the two systems, i.e., by 4–8 Cal. This is in good agreement with the fact that ΔF for the reaction keto→enol is known certainly to be greater than 6 Cal. and probably to be less than 14 Cal.[8]

CYCLOHEXADIONE 1,2

Three structures are possible.



XXIV XXV XXVI

The calculation is simpler than in the case of β-diketones since the enol forms of α-diketones do not form chelate rings, partly for steric reasons and partly on account of the impossibility of resonance within the ring. The resonance energy of the system O=C–C=O is not known, but presumably is not very different from that of C=C–C=O or of C=C–C=C. Consequently it would appear that the diketo form XXIV should be considerably more stable than the keto-enol XXV, which in turn should be more stable than the dienol XXVI. Actually, however, the compound appears to exist only in the keto-enol form. The reason for this discrepancy is probably to be found in the potential energy which results from the dipole repulsions of the carbonyl and the hydroxyl groups present, and which cannot be neglected in this case. The two

[8] J. B. Conant and G. H. Carlson, J. Am. Chem. Soc. **54**, 4054 (1932).

dipoles are close together and are held in the cis position by the ring formation. The magnitude of this effect cannot be determined with any accuracy on account of the uncertainty in regard to the position and orientation of the dipoles and the dielectric constant of the medium. A rough calculation, however, shows that the effect is in the right direction and is of the correct order of magnitude.[9] It is probable that similar effects are responsible for other discrepancies in quantitative comparisons noted above.

Diacetyl

This case differs from the preceding in that the molecule is not kept rigid by the presence of a ring. Hence the dipoles are free to orient themselves in the more stable trans position where their effect upon the stability of the molecule is relatively small. This is in accord with the fact that the molecule exists only in the diketo form.

Conclusion

The results which have been obtained for the simple tautomeric systems treated above are in complete qualitative agreement with experiment and furnish considerable justification for the semi-empirical treatment used. In only two cases (tricarbomethoxy methane and malonic ester) are the quantitative aspects of the calculation unsatisfactory. These two compounds differ from the rest in that, with them, enolization necessarily destroys the characteristic resonance of a carboxyl group. As has been pointed out, this fact makes the problem very complicated, and so it is not surprising that quantitative agreement is lacking at this point. It is doubtlessly significant, however, that the calculations for the two compounds are in good quantitative agreement with each other.

This same treatment could be extended to a number of other cases, but since its success depends upon the possibility of estimating the resonance energies of various groupings in the molecules concerned, it rapidly becomes of less value as the complexity of the resonating systems increases. For this reason it does not seem profitable to attempt the treatment of such cases as dibenzoylmethane, etc., where the presence of the phenyl groups complicates the problem tremendously. The success obtained with the simpler systems, however, makes it seem quite probable that these could also be treated satisfactorily by the same method if sufficient empirical data were at hand.

[9] For a somewhat similar calculation see H. M. Smallwood, J. Am. Chem. Soc. **54**, 3048 (1932).

Further Observations Concerning the Propagation of Sound in Nitrogen Tetroxide

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The absorption of sound in nitrogen tetroxide is discussed, and it is pointed out that absorption measurements should be capable of distinguishing whether a given absorptive region is due to failure of the dissociation reaction or of the heat capacity to follow the adiabatic cycle of the sound wave. Appropriate expressions for the absorption are derived from Einstein's theory, and are briefly discussed. An experimental method of determining the absorption maximum is described in which the temperature is varied at constant pressure and frequency. Under these conditions the acoustical variables are maintained very nearly constant. An attempt to detect the absorption maximum at 450.1 kc and 260 mm in nitrogen tetroxide was unsuccessful because of the inaccuracy of the absorption measurements. It is concluded that dispersion measurements provide at present an easier and more accurate method of investigating the acoustical properties of rapidly dissociating gases than measurements of the absorption coefficient. Occasion is taken to discuss the tube corrections applied to the previous dispersion measurements at greater length than was before considered necessary. Several corrections to the previous work are also appended.

INTRODUCTION

A RECENT communication from this laboratory[1] described measurements on the dispersion of sound in nitrogen tetroxide, and discussed in considerable detail an argument by which it was believed legitimate to interpret them as due to failure of the dissociation reaction to attain equilibrium in the sound wave. The chief purpose of this note is to extend the argument to acoustical absorption.

Our report has been followed by an article by Teeter[2] in which he devotes much space to unfavorable criticism of our work. We shall take this opportunity to answer such parts of Teeter's attack as appear to us to require discussion. The bulk of his criticism is, however, based on arguments which we consider that we have already adequately refuted, and it would serve no useful purpose to labor them further.

PART I. A DISCUSSION OF THE ABSORPTION OF SOUND IN DISSOCIATING GASES

The interpretation of absorption measurements in terms of dissociation rates

It has already been demonstrated[1] that suitable measurements of the dispersion of sound in a dissociating gas are capable of showing whether (a) the dissociation reaction, (b) the heat capacity, or (c) both the dissociation reaction and the heat capacity concomitantly are failing to attain equilibrium in the adiabatic cycle. This demonstration is not wholly free from objection, since it is based on a somewhat oversimplified picture of the conditions in the path of the sound-wave.[3] However, since it appears to represent the most satisfactory description of the phenomenon which is at present available, it is perhaps worth while to extend the treatment to absorption. In order to do this with as little complication as possible it is proposed to treat quantitatively only cases (a) and (b), leaving the somewhat more doubtful case (c) for later qualitative discussion. In developing the argument it will be convenient to review that previously given for cases (a) and (b) in connection with the dispersion.

Calling π and Δ the complex pressure and

* At present Fellow of the John Simon Guggenheim Memorial Foundation.

[1] Richards and Reid, J. Chem. Phys. **1**, 114 (1933).

[2] Teeter, J. Chem. Phys. **1**, 251 (1933).

[3] The assignment of a single characteristic time to the rate of adjustment of the heat capacity of a gas in which several quantum states are excited is at present without theoretical justification. See Bourgin, Phys. Rev. **42**, 721 (1933). It seems, nevertheless, to be a reasonable experimental expedient. See Richards and Reid, Nature **130**, 739 (1932). A more completely deduced description of the concomittant failure of dissociation reaction and heat capacity may, for the present, be expected to yield results of substantially the same form as that given here and in the previous communication.

density variations of the sound wave, the theory of Einstein[4] gives for a dispersive gas

$$\frac{\pi}{\Delta}=\frac{P}{\rho}\left[1+\frac{A_0+ifA_\infty}{B_0+ifB_\infty}\right] \quad (1)$$

where P and ρ are the equilibrium pressure and density, respectively, and

$$f\equiv\omega/\zeta \quad (2)$$

if ω is the frequency of the sound wave in radians, and ζ is the characteristic frequency of the process which produces the dispersion. In the case of a unimolecular reaction $\zeta\equiv k_1$, the rate constant. For a lag in heat capacity ζ is proportional to the number and effectiveness of the collisions which excite an active state of the molecule.[5] The quantities $1+A_0/B_0$ and $1+A_\infty/B_\infty$ represent the ratio of the isothermal to the adiabatic compressibilities when f sensibly vanishes and when f becomes sensibly infinite, respectively. The subscripts 0 and ∞ will be used in this sense throughout.

Since, as will later become apparent, the absorption due to the process characterized by ζ becomes negligible at very low and at very high frequencies, the real part (r.p.) of π/Δ becomes equal to the square of the phase velocity V. Thus from (1) the result is obtained that

$$V_\infty^2/V_0^2=B_0(B_\infty+A_\infty)/B_\infty(B_0+A_0)=Q^2 \quad (3)$$

and the useful abbreviation Q, which is intimately connected both with dispersion and absorption, is defined. The relationship (3) is alone sufficient to determine whether (a) or (b) has produced a given dispersive region, since the maximum change in velocity will be quite different for the two unless the dissociation heat is small. In the case of nitrogen tetroxide at 25°C and 260 mm, for example, the degree of dissociation α is about 0.3, and

Case (a)

$$\begin{cases} A_0=\left(\frac{2D}{T}-\bar{C}_0\right)\frac{1-\alpha}{1+\alpha}+R\left(\frac{2-\alpha}{\alpha}\right)\leqq 56.4 \text{ cal.} \\ A_\infty=A_D=R\leqq 2 \text{ cal.} \\ B_0=\frac{D^2}{RT^2}\frac{1-\alpha}{1+\alpha}+\bar{C}_0\left(\frac{2-\alpha}{\alpha}\right)\leqq 651 \text{ cal.} \\ B_\infty=B_D=\bar{C}_0\leqq 10 \text{ cal.} \end{cases}$$

according to the result of Einstein. This is on the assumption that the heat capacity continues to follow the wave without lag, as in case (a). For case (a) then, $Q^2\equiv Q_D^2=1.105$. In case (b) A_0 and B_0 remain unchanged, but the heat capacity alone drops out at high frequencies. To describe this it is sufficiently definite to write $\bar{C}_0=\bar{C}+\bar{C}_\omega$ where $\bar{C}_0$ represents the average heat capacity of the $N_2O_4-NO_2$ mixture at equilibrium and at constant volume, and $\bar{C}$ and $\bar{C}_\omega$ are its frequency-independent and -dependent parts, respectively. $\bar{C}_0$ is probably about 10 calories·mole^{-1}, and the utmost change of the heat capacity in regions of frequency which are at present accessible may be expected to be a drop to half this value. Thus $\bar{C}$ will be taken as 5 calories·mole^{-1}, and A_∞ and B_∞ become

Case (b)

$$\begin{cases} A_0\leqq 56.4 \text{ cal.} \\ A_\infty=A_c=\left(\frac{2D}{T}-\bar{C}\right)\frac{1-\alpha}{1+\alpha}+R\left(\frac{2-\alpha}{\alpha}\right)\leqq 59.1 \text{ cal.} \\ B_0\leqq 651 \text{ cal.} \\ B_\infty=B_c=\frac{D^2}{RT^2}\frac{1-\alpha}{1+\alpha}+\bar{C}\left(\frac{2-\alpha}{\alpha}\right)\leqq 623 \text{ cal.} \end{cases}$$

and for case (b) $Q^2\equiv Q_c^2\leqq 1.008$.

Thus it is seen that approximately ten times as much change in velocity results from case (a) as from case (b). A change of velocity greater than 0.4 percent, $((Q_c-1)\times 100)$, must, therefore, involve a partial failure of the dissociation reaction. It was an extension of this argument to case (c) by means of a simplified model for the heat capacity which made possible the calculation of rate constants from the measurements reported previously.[1]

[4] Einstein, Sitz. Ber. Akad., 380 (1920).

[5] Kneser, Ann. d. Physik **11**, 761 (1931), introduced the rate constant which we employed in the previous work, and shall continue to use here. Because the notation of Einstein has been retained wherever possible Kneser's β has been replaced by θ, both meaning identically the average lifetime of the excited molecule. Thus $\zeta\theta\equiv 1$ in our notation. In Kneser's, $\zeta\beta\equiv 1$.

In order to evaluate the corresponding maxima of the absorption coefficient it will be necessary to examine the structure of the complex pressure and condensation variations, π and Δ. For these Einstein[4] has written

$$\pi = \pi_0 e^{i\varphi} e^{i\omega(t-ax)} \tag{4}$$

$$\Delta = \Delta_0 e^{i\omega(t-ax)} \tag{5}$$

where the amplitudes are $\pi_0 e^{i\varphi}$ (complex) and Δ_0 (real), t is the time, x the distance in the direction of propagation, and a a complex quantity involving both velocity and absorption. It is apparent that the imaginary part of a becomes the only real part of the two exponents, and hence is a damping coefficient. If the symbol β denotes the absorption coefficient for the amplitude expressed as a reciprocal length, then a becomes

$$a = (1/V - i\beta/\omega) \tag{6}$$

where $2\pi V = \omega\lambda$ and $i = (-1)^{\frac{1}{2}}$. The familiar relationships, in which u denotes displacement in the direction of the wave normal,

$$\partial\pi/\partial x = -\rho\partial^2 u/\partial t^2 \quad \text{and} \quad \Delta = -\rho\partial u/\partial x \tag{7}$$

yield a wave equation of the usual form in which π/Δ is the square of a complex plane wave velocity, and has the value

$$\pi/\Delta = 1/a^2 = [V/(1 - i\beta V/\omega)]^2. \tag{8}$$

Eq. (1) is that from which the velocity and absorption of sound are to be determined in terms of the physical properties of the gas. It may readily be seen that the real part of π/Δ is more easy to obtain, from (1), than the real part of a (the real part of $(\Delta/\pi)^{\frac{1}{2}}$). Thus the convenient solution for the velocity is

$$\text{r.p.}\frac{\pi}{\Delta} = V^2\left\{\frac{1-\beta^2V^2/\omega^2}{(1+\beta^2V^2/\omega^2)^2}\right\}. \tag{9}$$

Similarly the imaginary part (i.p.) of Δ/π gives conveniently the absorption coefficient, as is apparent from (1), (6) and (8). Thus

$$\text{i.p. } \Delta/\pi = -i2\beta/\omega V. \tag{10}$$

Up to this point nothing has been added to the argument of Einstein.

If, now, the absorption coefficient for the intensity expressed as a reciprocal number of wave-lengths is introduced according to the usual definition

$$I_x = I_0 e^{-2\beta x} = I_0 e^{-hx/\lambda}$$

(10) becomes

$$h = -(2\pi V^2/i)(\text{i.p. } \Delta/\pi). \tag{11}$$

The imaginary part of the reciprocal of (1) gives

$$h = 2\pi V^2 \frac{\rho}{P}\left\{\frac{B_0(A_\infty+B_\infty)f - B_\infty(A_0+B_0)f}{(A_\infty+B_\infty)^2f^2+(A_0+B_0)^2}\right\}. \tag{12}$$

For the sake of convenience the rôle of absorption in the real part of Δ/π will be neglected, and it will be taken that

$$\text{r.p. } \Delta/\pi \leqq 1/V^2$$

and, consequently, from the reciprocal of (1), that

$$V^2 \leqq \frac{P}{\rho}\left\{\frac{(A_\infty+B_\infty)^2f^2+(A_0+B_0)^2}{B_0(A_0+B_0)+B_\infty(A_\infty+B_\infty)f^2}\right\}. \tag{13}$$

The approximation so introduced amounts to neglecting terms in h^2, or, practically, to setting

$$(\text{r.p. } \pi/\Delta)(\text{r.p. } \Delta/\pi) \leqq 1, \quad 2Q^2 \leqq Q^4+1$$

which, in the present condition of interferometric absorption measurements, will be without influence.[6] Substituting (13) into (12) gives finally

$$h \leqq 2\pi y\{(Q^2-1)/(1+Q^2y^2)\} \tag{14}$$

where y, which has been suggestively called the "relative frequency" by Luck,[6] is defined as

$$y \equiv fB_\infty/B_0 \equiv \omega B_\infty/\zeta B_0. \tag{14a}$$

Herzfeld and Rice,[7] Bourgin,[8] Henry[9] and

---

[6] Luck, Phys. Rev. **40**, 440 (1932) has carried through the solution for a dissociating gas without a heat capacity lag (case (a)) without making this approximation. Our (14) and (20) for this case are a slightly less accurate version of his

$$h_D = 4\pi\left[1+\frac{(1+Q_D^2y_D^2)^2}{(Q_D^2-1)^2y_D^2}\right]^{\frac{1}{2}} - \frac{1+Q_D^2y_D^2}{(Q_D^2-1)y_D^2}.$$

The approximation does not enter (15), and (16) has been given in both the approximate and the exact forms.

[7] Herzfeld and Rice, Phys. Rev. **31**, 691 (1928).

[8] Bourgin, Phil. Mag. (vii) **7**, 821 (1929).

[9] Henry, Proc. Camb. Phil. Soc. **28**, 249 (1932).

Kneser[10] have given similar equations for non-dissociating gases with variable heat capacity. The exposition used above was clearly implied by Einstein,[4] and has been here repeated only in order to give it somewhat more general significance.

The maximum of the absorption coefficient h may of course be found by setting $dh/d\omega=0$. It occurs at a frequency

$$\omega_{\max}=\zeta B_0/QB_\infty \tag{15}$$

and has the value

$$h_{\max}=4\pi[(Q-1)/(Q+1)]\cong\pi(Q-1/Q) \tag{16}$$

as Luck,[6] Henry[9] and Kneser[10] have pointed out in appropriate cases.

If (1) is written without regard for terms in h^2

$$\omega\cong(\zeta B_0/B_\infty)\{(V_\omega^2-V_0^2)/(V_\infty^2-V_\omega^2)\}^{\frac{1}{2}} \tag{17}$$

and $\omega_{\max}$ from (15) is substituted therein, there is obtained for the velocity at the point of maximum absorption

$$V_{\omega(\max)}^2=(V_\infty^2+V_0^2Q^2)/(Q^2+1)$$

which Luck,[6] Henry[9] and Kneser[5] have also reported.

Remembering that at 260 mm and 25°C in nitrogen tetroxide for case (a) $Q=Q_D=1.051$ and for case (b) $Q=Q_c=1.004$, the maximum absorption coefficient for the dissociation reaction $h_{D(\max)}$ is seen to be about 0.312 when the heat capacity remains fully active[11] and the maximum absorption coefficient for the heat capacity $h_{c(\max)}$ is approximately 0.030 if the dissociation reaction continues to follow the wave without lag. Here again case (a) gives about ten times the effect of case (b), and an experimental distinction between the two should easily be possible.

Turning now to case (c) where both heat capacity and dissociation contribute simultaneously to the absorption we shall make use of the same approximate model as was previously employed for the dispersion. It will be supposed that a single time constant θ is sufficient to describe the dispersive behavior of the heat capacity, and that the frequency dependence of the heat capacity conforms to the expression first suggested by Kneser[5] where $\bar{C}_v$

$$\bar{C}_v=\bar{C}+\bar{C}_\omega(1/(1+i\omega\theta))$$

is the contribution of the heat capacity to the complex velocity of sound at a frequency ω. Substituting this in the equation of Einstein in the usual way gives the complex velocity of sound as in Eq. (6) of the previous communication. For the present purpose the reciprocal of this may be written

$$\frac{\Delta}{\pi}=\frac{\rho}{P}\left\{\frac{k_1B_0-\omega^2\theta\bar{C}+i[k_1\omega\theta B_c+\omega\bar{C}_0]}{k_1(A_0+B_0)-\omega^2\theta(R+\bar{C})+i[k_1\omega\theta(A_c+B_c)+\omega(R+\bar{C}_0)]}\right\} \tag{18}$$

where A_0, B_0, A_c, and B_c have the values given above. The absorption coefficient in case (c) is then given by the expression

$$h_{DC}\cong 2\pi\left\{\frac{(k_1B_0-\omega^2\theta\bar{C})[k_1\omega\theta(A_c+B_c)+\omega(R+\bar{C}_0)]-(k_1\omega\theta B_c+\omega\bar{C}_0)[k_1(A_0+B_0)-\omega^2\theta(R+\bar{C})]}{(k_1B_0-\omega^2\theta\bar{C})[k_1(A_0+B_0)-\omega^2\theta(R+\bar{C})]+(k_1\omega\theta B_c+\omega\bar{C}_0)[k_1\omega\theta(A_c+B_c)+\omega(R+\bar{C}_0)]}\right\}. \tag{19}$$

This is not only unsightly, but has the disadvantage that it does not readily yield expressions of the type of (15) and (16). Nevertheless it must be briefly discussed in view of the experimental work which follows.

In case (a), when the heat capacity is without lag,

$$[\theta=0;\ y_D=(\omega/k_1)\cdot(\bar{C}_0/B_0)],\quad (19)\text{ reduces to}$$
$$h_D\cong 2\pi y_D\{(Q_D^2-1)/(1+Q_D^2y_D^2)\} \tag{20}$$

[10] Kneser, Ann. d. Physik **16**, 337 (1933). Kneser has given (14) for the case $B_0=C_i+C_a$ and $B_\infty=C_a$ in his notation. He has obtained (14) from the tangent of the phase angle φ by the approximation $2\pi\tan\varphi\cong h$. This may be seen to be identical with the approximation here introduced if $\tan\varphi$ is obtained from Eqs. (1) and (2) of our previous communication by neglecting terms in β^2.

[11] Luck (reference 6) was the first to point this out.

and in case (b) when the dissociation reaction is without lag,

$(k_1 \gg \omega,\ \theta^{-1};\ y_c = \omega\theta B_c/B_0)$, (19) reduces to

$$h_c \leqq 2\pi y_c\{(Q_c^2-1)/(1+Q_c^2 y_c^2)\}. \quad (21)$$

If the dissociation is so slow that it plays no part in the compressibility ratio ($k_1=0,\ f=\omega\theta$), (19) gives Kneser's expression[10] applied to a gaseous mixture of very particular properties:

$$h \leqq 2\pi f \frac{\bar{C}}{\bar{C}_0}\left\{\frac{Q^2-1}{1+Q^2(\bar{C}f/\bar{C}_0)^2}\right\}. \quad (22)$$

This case is without interest at present, since frequencies so high that the dissociation reaction has been wholly eliminated have not yet been employed to study nitrogen tetroxide. The magnitudes of the absorption maxima corresponding to (20) and (21) have already been discussed.

It appears best at present to limit the treatment of intermediate cases to a qualitative paragraph. In general, as might be expected, two absorption maxima, corresponding to two separate dispersive regions, appear when k_1 and θ^{-1} are different by more than two or three orders of magnitude. The two maxima are then roughly independent of each other. If k_1 is small compared to θ^{-1} the two separate peaks are of about the same height, corresponding to the two appropriate forms of (16). If, on the other hand, the heat capacity lag occurs at a lower frequency than that of the dissociation reaction, i.e., θ^{-1} is small compared to k_1, the absorption from the former is small, but that due to the latter considerably greater than (20) indicates, since the situation will then approximately be

$$h \leqq 2\pi \frac{\omega}{k_1}\frac{\bar{C}}{B_c}\left\{\frac{Q^2-1}{1+Q^2\omega\bar{C}/k_1 B_c}\right\}$$

where Q has a value greater than Q_D by an amount nearly proportional to the ratio $(\bar{C}_0/\bar{C})^{\frac{1}{2}}$. As k_1 and θ^{-1} approach each other the two absorption peaks merge into one which is conspicuously higher than either alone. It appears reasonable to suppose that in the limiting case where both dissociation and heat capacity fail at an identical frequency of sound the maximum of the absorption coefficient will be given by

$$h_{DC(\max)} \leqq \pi(Q-1/Q), \text{ where } Q=\left\{\frac{B_0(R+\bar{C})}{\bar{C}(A_0+B_0)}\right\}^{\frac{1}{2}}$$

If this is true, $h_{DC(\max)}$ will rise to 0.8 in nitrogen tetroxide at 25°C and 260 mm provided that $\bar{C}$ is reduced to 5 calories. In case the heat capacity fails at lower frequencies than the dissociation reaction or at the same frequency, $\omega_{D(\max)}$ will shift to higher frequencies in rough conformity to (15). An indirect consequence of this has already been illustrated by the dip in the curves of Fig. 1 of the previous communication.

An attempt to determine the absorption maximum by experiment

Since it appears from the previous discussion that the magnitude and position of the absorption maximum is influenced by heat capacity effects, it becomes reasonable to inquire whether absorption measurements may not conveniently supplement the information already gained from dispersion. Two publications have already reported observations concerning the absorption of sound in nitrogen tetroxide, but they do not, unfortunately, permit even qualitative conclusions.

Kistiakowsky and Richards[12] quote measurements of the logarithmic decrement coefficient of the d.c. plate current of the amplifier coupled to the magnetostriction oscillator as a function of pressure and frequency. This has been shown to be unreliable as a measure of absorption unless the conditions are very carefully controlled.[13] Their results will none the less be reproduced in Table I as the best at present available. It

TABLE I. *Decrement coefficient of the electrical reaction expressed as a reciprocal number of wave-lengths.*

Reprinted from Kistiakowsky and Richards.[12]

Frequency (kc)	P in mm 760	400	150
10	—	0.12	0.48
42	0.04	0.12	—
80	0.06	0.10	0.40

[12] Kistiakowsky and Richards, J. Am. Chem. Soc. **52**, 4661 (1930).

[13] Klein and Hershberger, Phys. Rev. **36**, 1262 (1930). Hubbard, ibid. **41**, 523 (1932).

is apparent that these coefficients can have little relation to h as defined above, since both at 10 kc and 80 kc and 150 mm they exceed the theoretical value of $h_{D(\max)}$. It appears rather that they represent some result of the mass reaction of the gas on the oscillator, and that, therefore, the amplitude of the oscillator is not independent of the position of the reflector. It must be pointed out that the 10 kc and 42 kc measurements are further invalidated by a damping coefficient which corresponds in magnitude to the tube-dispersion.[14] It seems, therefore, unwise to attempt to form any conclusions from them.

The observations of Teeter[2] are even less worthy of confidence. His electrical decrement coefficient at 25°C, 550 mm, and 54 kc is 0.82, which is some eight times as large as that reported by Kistiakowsky and Richards[12] at higher frequency and lower pressure (Table I above, 80 kc, 400 mm) and can, therefore, hardly bear any useful relation to the absorption coefficient. Teeter's failure to obtain evidence of transmission of sound above 54 kc is strikingly in contradiction both with the prediction of theory and with the observations of previous experimenters.[12, 1]

It is apparent that in both these investigations the comparison of measurements is made precarious by discontinuous changes in acoustical conditions as the pressure and frequency are changed. Each different oscillator introduces a new set of acoustical conditions, and each pressure change involves a significant alteration of the mass-reaction of the gas on the oscillator. A method of locating the absorption maximum by means free from these objections was, therefore, devised. By using the same oscillator and reflector for all measurements, and by holding the pressure constant, large changes of the type indicated above are eliminated. The gas may then be taken through its absorption maximum by varying the temperature, since the dissociation rate constant of nitrogen tetroxide varies with temperature in proportion to a factor $\exp -14{,}000/RT$. The density of the gas will, of course, vary inversely with the degree of dissociation, but over a small temperature range it seems reasonable to suppose this influence negligible.

[14] See Lamb, *The Dynamical Theory of Sound*, 2nd Ed., p. 196 (published by Arnold).

If the rate constant of 4.8×10^4 sec.$^{-1}$ for nitrogen tetroxide at 25°C and 260 mm is accepted from the dispersion measurements, and the constants A_0, B_0, $\bar{C}_0$ are taken as being those given in the previous section, $\omega_{D(\max)}$ will be about 470 kc at this temperature and pressure. This frequency must not be considered a prediction, since it is of course extremely sensitive to $\bar{C}_0$, and $\bar{C}_0$ has been arbitrarily given the value of 10 cal. It suffices, however, to show that the 450.1 kc oscillator already described (Fig. 4 and corresponding text of the work on dispersion, reference 1) is suitable to explore the absorption maximum at 260 mm in the neighborhood of 25°C. At 30°C the rate constant is about 6.7×10^4 and at 15°C about 2.6×10^4 at this pressure so that variation of the temperature between these limits should be sufficient to carry the gas through the absorption maximum provided that no heat capacity lag is present. The change in the absorption to be expected in this range is not, however, great, and it is difficult to predict whether measurements of the logarithmic decrement coefficient of the electrical reaction may be made with sufficient accuracy to detect it.

Table II summarizes a series of measurements at 451 kc and 260 mm, using this method. The first column, which is headed x/λ, is the distance from the reflector to the oscillator measured in wave-lengths. Thus the face of the oscillator corresponds to $x/\lambda=0$, and the first, third, fifth, etc., points of maximum electrical reaction, which do not correspond to an integral number of wave-lengths, are not reported. The relative electrical reaction is expressed as the ratio between the microammeter deflection at a point $x/\lambda=n$ divided by that at the point $x/\lambda=1$. Only 15 wave-lengths are recorded, although by suitable amplification nearly twice that number could be detected.

In argon, at a density approximating that of N_2O_4 at 25°C and 260 mm, the electrical reaction of the 451 kc oscillator decreased to 62 percent of its initial value after 15 wave-lengths.

That this attempt to locate the absorption maximum has been unsuccessful may be seen by looking horizontally across the table (for example at $x/\lambda=5$, 10 and 15). No significant diminution of the relative electrical reaction is noticeable at any temperature, and it is apparent that an

TABLE II. *Relative electrical reaction at various distances from the oscillator in nitrogen tetroxide at 260 mm, 451 kc, and various temperatures.*

x/λ	17.0°	18.3°	19.2°	20.0°	21.0°	22.0°	23.0°	24.1°	25.1°	26.1°	27.0°	29.0°
1	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2	0.64	0.61	0.66	0.72	0.76	0.64	0.60	0.59	0.68	0.73	0.64	0.63
3	.46	.46	.49	.48	.52	.45	.41	.46	.46	.49	.42	.48
4	.32	.31	.40	.37	.37	.30	.33	.28	.33	.36	.32	.33
5	.27	.23	.28	.27	.27	.23	.29	.21	.24	.24	.20	.25
6	.18	.18	.20	.21	.19	.16	.17	.17	.16	.18	.15	.18
7	.15	.11	.15	.16	.15	.11	.13	.12	.13	.12	.12	.13
8	.12	.08	.11	.12	.11	.08	.10	.08	.11	.11	.09	.10
9	.09	.06	.09	.10	.08	.07	.09	.07	.07	.09	.07	.07
10	.08	.05	.08	.08	.07	.05	.08	.06	.05	.06	.07	.06
11	.06	.03	.07	.06	.05	.03	.07	.05	.04	.05	.05	.05
12	.04	.02	.06	.05	.04	.03	.06	.04	.03	.04	.04	.04
13	.03	.01	.05	.04	.04	.03	.04	.03	.03	.03	.04	.04
14	.03	.01	.04	.03	.03	.02	.03	.03	.01	.03	.03	.02
15	.02	.01	.02	.03	.02	.01	.03	.02	.01	.02	.02	.02

accuracy which is greater by at least one order of magnitude is necessary to secure the desired information. The measurements have nevertheless been reported, since such scant conclusions as they permit are considered distinctly favorable to the interpretation of the dispersion which has previously been given.

It will be noticed that the intensity of the electrical reaction drops with fair uniformity to 2 percent of its initial value after 14 wave-lengths. This is in quantitative agreement with the prediction of Luck based on the supposition that the dissociation reaction alone is failing to follow the sound wave. Although the electrical decrement coefficient[15] and the acoustical absorption coefficient may be considered identical only under experimental conditions far more circumspectly controlled than those here described, this agreement is considered encouraging. A diminution to 2 percent after 14 wave-lengths is conspicuously less than that to be expected in case (c), if the dissociation reaction and all of the vibrational heat capacity are simultaneously failing in the sound wave, and $Q \equiv Q_{DC} = 1.14$. The possibility of case (b) has been conclusively eliminated by the dispersion measurements, and need not be discussed. Table II appears to indicate, therefore, that case (a), where the dissociation reaction alone is producing the absorption, is that which approximately obtains in nitrogen tetroxide at 25°C and 450 kc. Furthermore, the fact that decrement of the electrical reaction is not greater may be taken as support for the already well grounded conclusion that the tube correction in this apparatus is small. Such tentative conclusions as are permissible from Table II are, therefore, in full accord with those previously based on the far more quantitative dispersion measurements.

At present the heat capacity lag constants θ_{NO_2} and $\theta_{N_2O_4}$ must, therefore, be considered unknown.[16]

In closing the section which deals with absorption the situation may perhaps be summarized. It appears that at present measurements of the dispersion of sound are both easier to perform and more trustworthy in their implications than measurements of the absorption. It is, in fact, useless to attempt to

[15] A single decrement coefficient is not quantitatively satisfactory for describing the results in Table II.

[16] Teeter (reference 2) has stated that the dispersion which we have observed in nitrogen tetroxide may intelligibly be interpreted as wholly due to a heat capacity effect, and justifies this by a calculation in which a mean lifetime θ of 5×10^{-5} sec. is assigned to the $NO_2-N_2O_4$ mixture in rough analogy to Kneser's results on carbon dioxide. The calculation is made on the basis of an equation which is the dispersive analogue of (22) above, and is, therefore, applicable only when the dissociation reaction has been wholly eliminated from the adiabatic cycle. Since this cannot be the case under the conditions of our measurements, we disagree with his conclusion. Furthermore, if $\theta=5\times10^{-5}$ as Teeter supposes possible the corresponding absorption maximum would be at about 3 kc at 30°C and 260 mm from Eq. (15) above. This is not consistent with his own conclusion that the absorption maximum "comes somewhere near 700 kc." The basis for his conclusion is not given, and since neither temperature nor pressure are specified it cannot be compared with any deductions which are here supported.

obtain quantitative information concerning the absorption with the apparatus at our disposal in this laboratory. Nevertheless, it is to be hoped that some investigator experienced in absorption measurements, who has at his disposal a large number of calibrated quartz crystals, will ultimately bring this research to a positive conclusion. The position and magnitude of the absorption maximum can provide information of great theoretical interest concerning heat capacity effects in dissociating gases. This information is more difficult to obtain from dispersion measurements, for the reason that the position and magnitude of the absorption maximum indicate the value of V_∞, whereas dispersion measurements can obtain V_∞ only at much higher frequencies by direct measurement. If the dispersive region is compounded of two or more concomittant types of time lag the terminal velocity at high frequencies corresponding to each separate process may be clearly deducible from the absorption maximum although wholly inaccessible to direct measurement.

Part II. Supplementary Data Concerning The Dispersion Measurements Previously Reported

Further discussion of the tube-correction

The application of a tube-correction determined by experiment considerably increased the accuracy of the measurements of dispersion which were previously reported. We feel that the method by which this correction was obtained has already been sufficiently discussed, but that the account of its application is too brief to be immediately intelligible. Further, parts of Table III and all of Table IV were inadvertently printed with the measurements uncorrected, in direct contradiction to what was stated in the text. This has caused an obscurity concerning the tube correction which is wholly unnecessary[17] and we welcome an opportunity to dispel it. It must, however, be emphasized that nothing will be written in this section which was not previously considered in calculating the rate constants.

[17] Teeter (reference 2) has pointed out the inconsistencies in Tables III and IV, and has correctly estimated their origin.

Table III.

T°C	Linear frequency (kc)	Velocity (m·sec.$^{-1}$)	Linear frequency (kc)	Velocity (m·sec.$^{-1}$)	ΔV (m·sec.$^{-1}$)
1.0	9.265	170.8	92.07	172.8	1.8
1.0	9.341	171.4	92.14	173.0	
7.0	9.343	176.4	92.06	177.2	0.8
8.0	—	—	92.06	178.3	0.8
8.1	9.340	177.5	—	—	
10.0	9.331	179.2	92.02	179.9	0.7
13.9	9.336	183.05	92.00	183.6	0.55
25.0	9.298	195.3	91.89	195.7	0.3
25.0	9.298	194.8	91.89	195.0	
30.0	9.213	202.4	91.73	202.6	0.2
30.0	94.00	202.1	450.7	205.6	3.4
	94.00	202.0	450.7	205.5	
	94.00	202.2	450.7	205.4	

Table IV.

P (mm)	Frequency (kc)	Velocity (m·sec.$^{-1}$)	Frequency (kc)	Velocity (m·sec.$^{-1}$)	ΔV (m·sec.$^{-1}$)
			30°C		
342	94.00	198.4	450.7	200.7	2.3
260	94.00	202.1	450.7	205.4*	3.4
235	94.00	203.4	450.7	207.9	4.5
			25°C		
668	9.301	185.2	91.89	185.3	0.1
260	9.301	195.1	91.89	195.4	0.3
162	9.301	202.0	91.89	202.5	0.5
			1.0°C		
260	9.340	171.1	92.10	172.9	1.8
156	9.340	175.4	92.10	179.1	3.7
132	9.340	176.7	92.10	181.0	4.3

* This number is the average of the three corresponding measurements in Table III and should evidently be printed 205.5. It has not been corrected in order to facilitate comparison with the previous printing.

In order to be consistent with the text of the previous work, Tables III and IV should have been printed as they are here given. A careful comparison with the previous printing will show that the tube-corrections have been applied in the manner stated to all measurements in which the difference between the two velocities quoted did not accord with the sixth column and that, with the exception of a single misprint, the agreement is now complete and the sixth column unaltered. One further change has been made in reprinting the tables in that the sixth column

has been headed ΔV to show that it represents the difference in velocities at the two appropriate frequencies instead of $V_\omega - V_0$ as previously. These quantities may, of course, be quite different, but in the tables happen to be the same within experimental error.

Before describing in further detail the calculation of the rate constants from these measurements it should be emphasized that at 1°C and 132 mm (Table IV) ΔV is 4.3 m·sec.$^{-1}$, and the velocity at 9 kc, 176.7 m·sec.$^{-1}$. At 7°C and 260 mm (Table III), on the other hand, the velocity is almost identical at 9 kc and ΔV is only 0.8 m·sec.$^{-1}$. These two measurements alone are considered sufficient refutation of any fundamental objections to our conclusions based on the tube-correction, or a possible major effect due to heat-capacity dispersion. It was not previously considered necessary to emphasize this point.

The calculation of rate-constants from these measurements will now be considered in greater detail. It has already been stated that the chief cause for numerical disagreement between the measured velocity of sound and that calculated from Einstein's theory lies in uncertainty concerning the density of the gaseous mixture. A method of calculation was, therefore, employed in which the pressure and density were wholly eliminated by the use of the velocity of sound at very low frequency. This was effected by writing, in the notation of this paper,

$$k_1 = (\omega \bar{C}_0/B_0)\{(V_\infty^2 - v_\omega^2)/(v_\omega^2 - v_0^2)\}^{\frac{1}{2}}$$

where the symbol v now refers to an experimentally determined phase velocity. V_∞^2 was calculated from the experimental velocity by means of the relation

$$V_\infty^2 = v_0^2\{B_0(\bar{C}_0 + R)/C_0(A_0 + B_0)\}.$$

This procedure is applicable quite generally to measurements on the dispersion of sound. Not only does it very largely remove systematic errors because of imperfections of the gas, incorrect determination of its thermodynamic constants, etc., but it makes possible the calculation of reasonably accurate time lag and dissociation rate constants when the measured values of the velocity accord relatively, but are greatly different from their values calculated from theoretical considerations alone.

For this reason no great concern was felt when the measured and calculated velocities differed by as much as 2 m·sec.$^{-1}$. The tube corrections were applied merely to make ΔV obtained from $V_{92} - V_9$ a self-consistent quantity, and similarly to make comparable the quantity $V_{451} - V_{94}$. The method of calculation made it unnecessary that V_{94} and V_{92} should be comparable, or that either should agree with the calculated velocity to anything like the precision claimed for ΔV. It will be remarked, for instance, that at 30°C and 260 mm V_{92} is 202.6 m·sec.$^{-1}$, and V_{94}, 202.1 m·sec.$^{-1}$. A difference of this kind is to be expected, for no effort has been made to apply a tube-correction which will make the two comparable. It is further a matter of indifference which of the two is accepted provided that the calculation of the rate constant is consistently made. There are two reasonable methods of making the calculation, (A) to add 0.5 m·sec.$^{-1}$ to V_{94} and to V_{451} to make them comparable to V_9 and V_{92}, or (B) to subtract 0.2 m·sec.$^{-1}$ from V_{94} to account for the dispersion and to use this for V_0. The result obtained is the same within experimental error

$$\text{(A)}\quad k_1 = \frac{\omega \bar{C}_0}{B_0}\left\{\frac{(211.5)^2 - (206.0)^2}{(206.0)^2 - (202.4)^2}\right\}^{\frac{1}{2}} = 1.249\,\frac{\omega \bar{C}_0}{B_0}$$

$$\text{(B)}\quad k_1 = \frac{\omega \bar{C}_0}{B_0}\left\{\frac{(211.0)^2 - (205.5)^2}{(205.5)^2 - (201.9)^2}\right\}^{\frac{1}{2}} = 1.250\,\frac{\omega \bar{C}_0}{B_0}.$$

Nevertheless an attempt was made to ascertain whether V_{92} or V_{94} was the more worthy of confidence by measuring the velocity of sound in argon, a quantity which can be calculated with some precision since $C_P/C_v = 1.667$ on theoretical grounds. On this basis V_{92} appeared the more accurate, as already reported.

One further aspect of this argument which appears to have caused confusion is the determination of the difference $V_9 - V_0$, because of the entry of the gas into the dispersive region. This was shown negligible in all cases by a calculation at 1°C and 260 mm. Here $V_\infty \cong 177.9$, $V_{92} = 172.9$, $V_9 = 171.1$ m·sec.$^{-1}$. k_1 is, therefore, approximately

$$k_1 \leqq \frac{2\pi(9.2\times10^4)\bar{C}_0}{B_0}\left\{\frac{(177.9)^2-(172.9)^2}{(172.9)^2-(171.1)^2}\right\}^{\frac{1}{2}} \leqq 7.0\times10^3.$$

In order to find if V_9 is appreciably different from V_0 the calculation is then made

$$7.0\times10^3 = \frac{2\pi(9.3\times10^3)\bar{C}_0}{B_0}\left\{\frac{(177.9)^2-(171.1)^2}{(171.1)^2-V_0^2}\right\}^{\frac{1}{2}}$$

and it is found that $V_9 - V_0 = 0.03$ m·sec.$^{-1}$ and therefore inconsiderable. It was on this basis that we have written, "The accuracy of the rate constants in Table VI must now be considered. It may be shown from these by (9)" [the equation used above] "that the velocity of sound at very low frequency at 1°C is less than 0.1 m·sec.$^{-1}$ below that quoted at 9 kc. Error from this cause is, therefore, eliminated."

One further point concerning the tube-correction requires more extended discussion. We have suggested that the tube-correction may undergo a change in the dispersive region of frequency, since a literal application of the Helmholtz-Kirchhoff expression for the damping of plane waves in small tubes appears to indicate a certain increase in damping as the compressibility ratio of the gas is increased. We were content to show that this effect, if it occurred, would be negligible. Teeter has, however, based a criticism of our work on this subject, and the argument must, therefore, be more fully stated.

For this purpose it will be sufficient to use a very approximate statement of the Helmholtz-Kirchhoff relation. The tube correction for a particular diameter of tube, a particular gas, and a particular frequency will be called τ_ω when $V_\omega - V_0 \doteq 0$. If the conditions in the gas are changed so that $V_\omega - V_0$ becomes appreciable (for example by lowering the temperature or pressure) the Helmholtz-Kirchhoff expression leads to the expectation that a larger tube-correction τ_ω' would be found.[18] A much simplified approximation

$$\tau_\omega'/\tau_\omega \leqq V_\omega^2/V_0^2$$

reproduces the numerical implications of the Helmholtz-Kirchhoff expression with quite sufficient accuracy for the present purpose. Since V_ω^2/V_0^2 might change from 1.00 to 1.25 from the beginning to the end of the dispersive region an increase of 0.5 m·sec.$^{-1}$ might occur in a tube-correction of 2.0 m·sec.$^{-1}$. Since $V_\infty - V_0$ is about 10 m·sec.$^{-1}$ this represents a 5 percent change in the differences in velocity due to the tube-correction. With a tube-correction of 2 m·sec.$^{-1}$, then, the tube-correction will be approximately $\tau_\omega + 1.05(V_\omega - V_0)$, and will equal τ_ω for small values of $V_\omega - V_0$.

This estimate of the error may easily be shown, however, to be unnecessarily generous when applied to our measurements. In the tubes which we used the tube-correction was always less than 2 m·sec.$^{-1}$ at high frequencies, and only at high frequencies did $V_\omega - V_0$ become of important magnitude. At lower frequencies the tube-correction was great, but $V_\omega - V_0$ small enough to be negligible. An estimate of the error possibly introduced by change in the tube-correction is appended in Table V. V_ω^2/V_0^2 from appropriate measurements gives the column headed τ_ω'/τ_ω. The column headed $2\tau_\omega$ is the most probable value of the tube-correction when $V_\omega - V_0 = 0$ multiplied by two for good measure. The last column shows twice the error probably introduced by neglecting the possible change in the tube-correction in the dispersive region, and has been called the maximum error.

TABLE V. *Estimate of error introduced into previous measurements on dispersion by a possible change in the tube-correction.*

Conditions	τ_ω'/τ_ω	$2\tau_\omega$ m·sec.$^{-1}$	Maximum error $2(\tau_\omega'-\tau_\omega)$ m·sec.$^{-1}$
9 kc 1°C 260 mm	1.001	0.8	0.001
92 kc 1°C 260 mm	1.002	2.0	0.004
94 kc 30°C 260 mm	1.010	0.4	0.004
451 kc 30°C 260 mm	1.050	0.6	0.030

It is perhaps sufficient comment on this table to repeat that our claimed error was never less than 0.2 m·sec.$^{-1}$. We can therefore only reiterate our previous statement that the error introduced by neglecting the tube-correction change "is

[18] Since it is desired only to find the maximum error due to this change the legitimacy of such a literal interpretation of the expression for the tube-dispersion need not be discussed.

believed to be considerably inferior to that due to other causes." We do not understand on what grounds Teeter has disregarded this statement without attempting to refute it.

In concluding this section it should be noted that nothing which has been said above must be considered as *a fortiori* justification of our previous work, for it is an amplification of an argument already indicated. Neither must it be considered a defense, for our previous position has not been attacked, but wholly disregarded. We must express our regret that it has been necessary to discuss in such intimate detail matters of very small scientific interest.

The effect of deviations from ideal gas laws and of absorption on rate constants computed from dispersion measurements

We had previously supposed that the approximate agreement of V_0 and of dV_0/dP at 260 mm with the values obtained from Einstein's equation[19] combined with the method we have used in calculating the rate constants, removed any serious error due to non-ideality of the mixed gas. Teeter's demonstration, from the argument given by Luck, that this is not necessarily the case, is therefore welcome. His estimate of the error introduced at the absorption maximum is, however, conclusive only if Q $(=V_\infty/V_0)$ is a measured quantity. When, as in the case we have discussed, V_∞ is calculated, k_1 at the absorption maximum becomes from (3) and (15)

$$k_1=\omega\{\bar{C}_0(\bar{C}_0+R)/B_0(A_0+B_0)\}^{\frac{1}{2}}$$

and A_0 is also involved. Luck has already pointed out that the coefficients involved in the calculation of A_0 from his development of the theory cannot at present be estimated. It might, of course, be argued that the experimental agreement of V_0 with the result calculated when using ideal gases indicates that A_0 and B_0 are affected equally by departures from ideal behavior. This would introduce, at the absorption maximum, about the error which Teeter has estimated, but would involve as a corollary our original assumption that rate constants calculated from small values of $V_\omega-V_0$ are without error due to this cause. It appears impossible, at present, to give this question a more satisfactory answer. This is especially the case because experimental determinations of the density are lacking below 25°C and, even above this temperature, do not define the value of P/ρ with accuracy sufficient for acoustical purposes.

Teeter has pointed out that errors in rate constants due to departure from ideal behavior are of opposite sign to those due to the neglect of the effect of absorption on the velocity. He has estimated the latter effect variously as 20 percent and as 4 percent.[20] We agree with the latter of these two estimates. In the only case of quantitative importance for our argument, that at 30°C, 451 kc and 260 mm, this effect may readily be calculated. Here Q, when using the average value from the "maximum" and "minimum" heat capacity, is about 1.048, $\bar{C}_0$ is 9.83 and B_0 (using $\alpha=0.359$, $D=14.0$ kg cal·mole^{-1}) is 661. This gives $h=0.267$ from (14). Then

$$\frac{v_\omega}{V_\omega}=\left\{\frac{1-(h/4\pi)^2}{[1+(h/4\pi)^2]^2}\right\}^{\frac{1}{2}}=0.99933$$

where v_ω is the measured velocity of sound $(2\pi v_\omega=\omega\lambda)$ and V_ω is the square root of the real part of π/Δ. This equation is of course derived from (9), and was first suggested by Luck.[5] The measured velocity of sound is, therefore, about 0.14 m·sec.$^{-1}$ below that given by r.p. π/Δ under these conditions. The relation of the true rate constant k_1 to that calculated neglecting the absorption k_R is then

$$\frac{k_1}{k_R}=\left\{\frac{V_\infty^2-V_\omega^2}{V_\omega^2-V_0^2}\right\}^{\frac{1}{2}}\left\{\frac{v_\omega^2-V_0^2}{V_\infty^2-v_\omega^2}\right\}^{\frac{1}{2}}=1.04$$

which agrees with Teeter's estimate. This is well within the experimental error which we have allowed, and is probably overbalanced by the error due to the departure of the gas from ideal behavior.

[19] This is well illustrated at 25°C by Teeter's Fig. 5. It should perhaps be pointed out that our measurement at 9 kc and 668 mm has been incorrectly plotted in this figure, although it is correctly quoted in the corresponding table. The error is minor, but it gives an unmerited appearance of incoherence to our work.

[20] Teeter, reference 2 and J. Am. Chem. Soc. **54**, 4111 (1932).

There appears to be no reason at present for revision of the rate constants which we have given previously from either of the causes discussed in this section.

Corrections of the previous communication

Unfortunately, a number of misprints and one actual error appear in the previous work.

The following corrections should be noted. The argument was developed throughout by using the correct and not the incorrect statements.

Page 115. Lines 13 and 14, left-hand column. The real part of the two exponents should be $-\beta x$ and not $-\beta$.

Page 116. Lines under Eq. (8) should read "γ is the ratio of the isothermal to the adiabatic compressibilities."[21]

Page 117. Eq. (9) should read[22]

$$k_1=\omega\left\{\frac{\bar{C}_0RT^2\alpha[2+\alpha(1-\alpha)]}{(2-\alpha)\{\bar{C}_0RT^2[2+\alpha(1-\alpha)]+D^2\alpha(1-\alpha)\}}\right\}\left\{\frac{V_\infty^2-V_\omega^2}{V_\omega^2-V_0^2}\right\}^{\frac{1}{2}}.$$

The calculations of the rate constants were made using the convenient grouping of constants printed by Gruneisen and Goens,[23] after a comparison with a properly reduced version of our (8). It may easily be verified that the rate constants we have given are free from the error involved in (9) as originally printed.

Page 117. Fig. 2 should have as abscissae $\infty\ \bar{4}\ \bar{5}\ \bar{6}\ \bar{7}\ 0$ making the point of inflection of the $\omega=10^5$ curve nearly at $\theta=\bar{5}$.

Page 119, 22nd line from top, right-hand column, should read "pure plane sinusoidal wave."

Page 123. Tables III and IV should read as printed above.

Page 123, lines 17–15 from bottom, right-hand column. The statement "The second equation of (3) neglects the influence of temperature and pressure on the degree of dissociation" is nonsense, and should be deleted.

Page 125, line 10, right-hand column, should read

$$V_\infty=(V_0^2\gamma_\infty/\gamma_0)^{\frac{1}{2}}$$

and it should be emphasized that V_0 refers to the experimental velocity.

Page 127. The formula for $1/\Lambda$ should omit M_2 from the denominator of the last term on the right.

The only systematic error which Teeter has pointed out must now be discussed. We have incorrectly used 14.6 kg·cal. as the heat of dissociation at constant volume derived from the measurements of Verhoek and Daniels[24] instead of the correct value of 14.0 kg·cal. The effect of this error is to make the rate constants previously reported uniformly about 9 percent too low. It is not surprising that this figure falls within the estimated experimental error of 10 percent because uncertainty concerning the dissociation heat was of course included in the estimate. Evidently it is necessary to consider that the dispersion measurements indicate a reaction rate constant of 5.3×10^4 sec.$^{-1}$ at 260 mm and 25°C, and similarly to raise by 9 percent all the rate constants quoted. The exact absolute values of these constants have, however, little contemporary importance. It is more significant that the activation energy which was previously given (13.9 ± 0.9 kg·cal.) is unchanged, and is now so near to the most probable value of the dissociation heat (14.0 kg·cal.) that the agreement between the two must be considered in part fortuitous.

[21] Teeter has pointed out this slip. By stating that we have the ratio inverted he is apparently, however, referring to (8) which is correctly printed. His statements that $\gamma=C_P/C_v$ and that it is a complex have no relation to anything we have said. It is necessary to call attention to this since, as he has not reprinted γ, the impression is distinctly misleading. The relation between Einstein's β and Luck's l is of course $\beta l\equiv1$.

[22] We are indebted to Teeter for calling attention to this error.

[23] Gruneisen and Goens, Ann. d. Physik **72**, 193 (1923).

[24] Verhoek and Daniels, J. Am. Chem. Soc. **53**, 1250 (1931).

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Spectroscopic Evidence for the Molecule PN

In a discharge through air in a tube which previously had been used with phosphorus we found a rather extensive system of simple diatomic bands in the region 2400–2900A which had not been recorded before. Further experiments showed that these new bands do not occur in a similar discharge through air or nitrogen *without* the presence of phosphorus. On the other hand they have never been observed in discharges through phosphorus vapor alone. The bands do however occur strongly in a discharge through a *mixture* of pure nitrogen and pure phosphorus vapor (at the same time strong clean-up occurs). We therefore conclude that the band system is due to the diatomic molecule PN. This is confirmed by a closer analysis of the band system (see below).

A search through the literature showed that the only well-known compound of phosphorus and nitrogen is P_3N_5, discovered by Stock. In addition Moldenhauer[1] found several years ago that in a discharge through nitrogen and phosphorus a yellow powder is formed which contains equal amounts of phosphorus and nitrogen and which is remarkably stable. The free molecule PN in the vapor phase has not been observed up until now. The above experiments show that this molecule at least temporarily exists in gas discharges through a mixture of N_2 and P_4.

We have so far measured the heads of 24 bands. These are represented rather accurately by the formula

$$\nu = 39{,}699.3 + (1094.75v' - 7.25v'^2) - (1329.38v'' - 6.98v''^2).$$

The fine structure of the bands is fairly well resolved on our plates (second order of 3 m grating). Each band consists of one P, one Q and one R branch, thus the system is a $^1\Pi \rightarrow {}^1\Sigma$ transition (most probably the lower state is $^1\Sigma$). Therefore the remote possibility that the system is due to PO or CP, which might have been present as impurities, is excluded, because these can only have doublet (or quartet) terms. A preliminary rotational analysis gave the constants:

$$B_0'' = 0.78 \text{ cm}^{-1}, \quad B_0' = 0.73 \text{ cm}^{-1}; \quad r_0'' = 1.49\text{A}, \quad r_0' = 1.54\text{A}.$$

These, as well as the vibrational constants (see the above formula) are similar to those for the corresponding systems of CS and SiO, as is to be expected. This is a further argument for PN as carrier of the band system.

It seems probable that the lower electronic level $^1\Sigma$ of the bands is the ground state of the molecule. The energy of dissociation of this state comes out by linear extrapolation to be 7.8 volts. This of course is to be regarded as an upper limit.

A full report of this work will appear shortly elsewhere. A further investigation of this molecule, both in emission and absorption, seems promising especially with respect to a comparison with N_2 and P_2.

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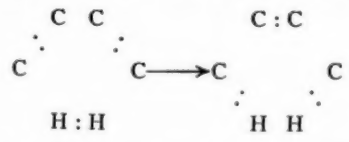
August 19, 1933.

[1] W. Moldenhauer, Chem. Ber. **59**, 926 (1926).

1–4 Addition and Subtraction Reactions in Hydrocarbon Chemistry[1]

Eyring, Sherman, and Kimball[2] have treated 1–4 addition to conjugate double bonds by means of the model



where each dot represents an electron considered in the calculations. Using 74.5, 92, and 102.4 kcal. for the strengths of the C–C, C–H, and H–H bonds, they find an activation energy of 64 kcal. for the addition of hydrogen to conjugate double bonds. These bond strengths, however, give a heat of reaction of only 7.1 kcal., whereas heats of combustion require 32 kcal. This difference must

[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Eyring, Sherman and Kimball, J. Chem. Phys. **1**, 586 (1933).

be made up mainly by decreasing the strength of C−C, which denotes actually the difference between C=C and C−C. The calculated heat of activation then will be somewhat lower, probably about 50 kcal. Sherman and Eyring,[3] using a more suitable value for C=C, previously calculated an activation energy of 51.5 kcal. for the hydrogenation of ethylene. Here again the reaction is approximately 30 kcal. exothermic. The theoretical activation energy for either 1–2 or 1–4 dehydrogenation is thus 80 kcal.; the experimental value in the former case is 70 kcal., and a similar figure seems reasonable for the 1–4 reaction.

There is also a second possible type of 1–4 dehydrogenation:[4]

$$CH_3CH_2CH_2CH_3 \longrightarrow H_2+CH_2:CH_2+CH_2:CH_2.$$

This type actually corresponds somewhat more closely to the six-electron model than does the production of butadiene from butylene. It is approximately 20 kcal. more endothermic, however, since it takes more energy to break C−C than it does to reduce C=C to C−C. The difference in activation energy will be considerably less than 20 kcal.; accurate predictions are impossible, but it appears worth while to look for this type of decomposition of hydrocarbons with a straight chain of at least four carbon atoms. By analogy with the 1–2 case, we shall expect to find 1–4 loss of methane, ethane, etc., and also, when the parent hydrocarbon is large enough.

The recent work of Frey and Hepp[5] may be interpreted as showing that this type of reaction occurs. For *n*-butane itself the evidence is somewhat conflicting; 1–4 dehydrogenation may constitute up to 5 percent of the primary reaction. For *n*-pentane the data may be interpreted as indicating the following primary products.

	Percent		Percent
$H_2+C_5H_{10}$.....	5.2	$H_2+C_2H_4+C_3H_6$.....	18.5
$CH_4+C_4H_8$.....	30.9	$CH_4+C_2H_4+C_2H_4$....	12.2
$C_2H_6+C_3H_6$....	31.5		
$C_3H_8+C_2H_4$....	1.7		
	69.3		30.7

For *n*-hexane, 60 percent of the reaction seems to go by way of 1–4 unsaturation, and only 40 percent by 1–2. For 2-methylbutane and 2,3-dimethylbutane, 20 percent and 12 percent, respectively, of the total reaction involves 1–4 unsaturation. These results have been interpreted by Frey and Hepp, and by Rice,[6] in terms of Rice's free radical mechanism. A detailed analysis shows that the free radical theory and the present unsaturation theory predict the same products in approximately the same yields. For very long chains it would be necessary to postulate 1–6, 1–8, etc., unsaturation, with resulting scission into four, five, or more primary products, to match exactly the free radical predictions; there is no experimental evidence on this point. The free radical mechanism does predict a decrease in the mean molecular weight of the primary products as the pressure is lowered. On the unsaturation theory such a decrease should not occur in the region where the reaction rate is strictly first order. No existing data even approach being good enough to make this test.

There is little doubt that free radicals are formed from metal alkyls, and in a few other cases where there are unusually weak bonds, but it appears possible to give a nearly complete account of the decomposition reactions of organic chemistry in terms of 1–1, 1–2, and 1–4 unsaturation. It is hoped to discuss this subject in more detail later. For the present, it is sufficient to mention a few further examples of 1–4 unsaturation: the formation of ethylene and butadiene from cyclohexene, of carbon dioxide and allyl alcohol from glyceryl oxalate, and of methane, ethylene, and formaldehyde or hydrogen, ethylene, and acetaldehyde from ethyl ether. In this last case, the chief reaction is 1–2 splitting to ethane and acetaldehyde.

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August 24, 1933.

[3] Sherman and Eyring, J. Am. Chem. Soc. **54**, 2561 (1932).

[4] Cf. Gault and Hessel, Ann. chim. [10] **2**, 376 (1924), who postulated a similar process to account for the production of hydrogen in the pyrolysis of hexadecane.

[5] Frey and Hepp, Ind. Eng. Chem. **25**, 441 (1933).

[6] F. O. Rice, J. Am. Chem. Soc. **55**, 3035 (1933).

[7] Associate physical chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

On the Concentration of Deuterium by Electrolysis

Bleakney and Gould[1] have raised the question as to the reason for the low concentration of deuterium in commercial electrolytic cells as is shown by the analysis of hydrogen obtainable commercially. They point out that this low concentration would imply that this tank hydrogen has all come from apparently new cells.

The specific gravity of water which was distilled from electrolyte which was kindly furnished by the Pittsburgh plant of the Burdett Hydrogen and Oxygen Company has been obtained. This water was carefully purified by distillation through a still which is used for the production of conductivity water, and then deaerated. The specific gravity was obtained by means of a buoyancy balance similar to that described by Lewis and Macdonald.[2] Six cells were sampled and the specific gravity obtained was 1.000013 compared to ordinary conductivity water at 18.2°C. The results on all samples agreed to about one part in a million.

The cells from which the electrolyte was taken had been in operation for about five years without the electrolyte having been renewed. A simple calculation showed that

[1] Walker Bleakney and Austin J. Gould, Phys. Rev. **44**, 268 (1933).

[2] G. N. Lewis and R. T. Macdonald, J. Chem. Phys. **1**, 341 (1933).

the amount of water electrolyzed during this period of operation was about 30 times the amount the cells contained. It would appear from this calculation that these cells had been in operation for a long enough period of time to have nearly reached their equilibrium concentration, this equilibrium concentration being given by the relation deduced by Lewis and Macdonald[2] as $1/\alpha$ times the concentration of the water added to the cells, where α is the separation factor. This separation factor α must be a function of the temperature at which the electrolysis is taking place, as is shown by the following calculation.

If we assume Dalton's law of partial pressures to apply, the fractional part of a mole of water vapor removed per mole of water electrolyzed will be $3P_W/2(P_A-P_W)$, which quantity we shall call ϵ. Where P_W is the partial pressure of water vapor at the temperature T, and P_A is the atmospheric pressure. Thus the amount of water removed from the cell will be $1+\epsilon$ moles per mole electrolyzed. If δ_1 and δ_2 represent the amounts of H^1 and H^2 evolved per mole of hydrogen produced, and C_1 and C_2 are the respective concentrations of the two kinds of hydrogen in the electrolyte expressed as mole fractions, then $\delta_2C_1/\delta_2C_2=\sigma$ is the true electrolytic separation factor. The hydrogen lost by vaporization of the water will be ϵ moles per mole electrolyzed. Thus the α of the Lewis and Macdonald[2] equation obviously becomes,

$$\alpha=(\delta_2+\epsilon C_2)C_1/(\delta_1+\epsilon C_1)C_2.$$

Assuming Bleakney and Gould's[1] value (1 part in 5000) for the abundance of deuterium in ordinary water, and using Lewis and Macdonald's[3] value for the density of pure deuterium oxide, the value of σ can be calculated if we further assumed that the electrolytic hydrogen analyzed by Bleakney and Gould[1] came from a typical old cell of the type which was referred to above. This calculation gives a value of 0.12 for σ which would agree fairly well with the provisional value of 0.10 given by Urey.[4] By taking this value (0.12) for σ and calculating α for this cell, ($T=160°$F) the value of α obtained is 0.37. The experimental value of α for such a cell will be considerably higher than this calculated value, due to the fact that evaporation from the surface of the electrolyte, which will be considerable at this temperature, has not been taken into account in the calculation. Calculating for Lewis and Macdonald's[2] cells ($T=35°$C) the value of α obtained is 0.16 which is in fair agreement with the experimental value of 0.20 when it is considered that the mechanical loss of water during the electrolysis is neglected, which loss would tend to increase the calculated value of α.

From the above considerations it would appear that commercial cells which are run hot in order to attain high power efficiency must necessarily have a low equilibrium concentration of deuterium, and also that the hydrogen produced by such cells will have a correspondingly low concentration of the heavier isotope.

The author is indebted to Dr. J. G. Aston of the Chemistry Department for the use of the thermostat and conductivity still which made the determinations of specific gravity possible.

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Pennsylvania State College,
August 29, 1933.

[3] G. N. Lewis and R. T. Macdonald, J. Am. Chem. Soc. **55**, 3057 (1933).

[4] H. C. Urey, Rev. Sci. Inst. **4**, 425 (1933).

The Effect of Water Containing the Isotope of Hydrogen upon Fresh Water Organisms

Since the announcement by Washburn and Urey[1] that in electrolysis the residual water is enriched in heavy hydrogen, there has been a greatly increased interest in the separation and properties of isotopes. That the chemical reactivity of two isotopes with such different atomic weights would differ very considerably was of course clear, and the opinion that heavy water would have striking biological effects was generally held.

Lewis[2] has recently demonstrated that the seeds of tobacco will not germinate in pure H^2H^2O whereas seeds in ordinary distilled water sprouted within two days. We have recently performed a series of experiments to test the action of heavy water upon the vital activities of fresh water organisms. Our results are briefly summarized as follows:

(1) Water containing the isotope of hydrogen in high concentration (92 percent) was found to be toxic for the animals tested.

(a) Tadpoles of the green frog Rana clamitans died within an hour after being placed in the water. Control animals in 30 percent heavy water, and in ordinary distilled water, remained unaffected at the end of twenty-four hours.

(b) The common aquarium fish Lebistes reticulatus is killed by the water within an interval of two hours. Neither 30 percent heavy water, or distilled water exerted an effect over a twenty-four hour interval.

(c) Flatworms, planaria maculata are destroyed within three hours in the 92 percent heavy water, but were uninjured by the 30 percent heavy water over a period of three days.

(d) The protozoan, paramoecium caudatum is killed by the 92 percent heavy water within 48 hours. Water containing 15–20 percent of the heavy isotope of hydrogen did not affect the organisms during a three day interval. Paramoecium showed more resistance to the toxic action of the water than the highly organized animals studied.

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W. W. Swingle
H. Eyring
A. H. Frost

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Princeton University,
September 15, 1933.

[1] Washburn and Urey, Proc. Nat. Acad. Sci. **18**, 496 (1932).

[2] G. N. Lewis, J. Am. Chem. Soc. **55**, 3503 (1933).